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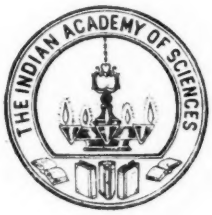

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A STUDY OF THE BENZOIN REACTION.

VI. The Effect of Temperature Variation on the Benzoin Reaction.

By B. F. Ferreira and T. S. Wheeler.

(From the Department of Chemistry, The Royal Institute of Science, Bombay.)

Received July 22, 1938.

For some time past this Laboratory has been engaged on a study of the kinetics of the benzoin reaction between solid potassium cyanide and benzaldehyde.[1] It has been shown that when pure potassium cyanide and pure benzaldehyde react, two concurrent reactions take place: a fast homogeneous autocatalytic reaction, between benzaldehyde and a trace of potassium cyanide dissolved in it, which requires the presence of benzoin; and a slow heterogeneous reaction between benzaldehyde and the solid potassium cyanide. The slow heterogeneous reaction is subject to inhibition by compounds such as potassium chloride, iodine and quinone. This paper comprises a study of the effect of temperature variation between 60° C. and 120° C. on the two reactions involved; previous work has been done at 100° C.

Experimental Technique and Discussion of Results.

The analytical methods and the general technique have been described in the previous papers. Merck's purest benzaldehyde, pretreated with potassium cyanide (Part V, *loc. cit.*, p. 614) and Kahlbaum's purest potassium cyanide dried at 110° C. at 2 mm. pressure for 2 hours were used. Water was employed in the thermostat up to 100° C. and above that glycerol. The temperature was kept constant to within 0·3° C.

The approximate solubility of benzoin in benzaldehyde was determined as it was required in the examination of the results. The method employed involved observation of the clouding-points of benzoin solutions of known strength in benzaldehyde. Table I summarises the solubility results.

Figs. 1, 2 and 3 give the experimental observations on the production of benzoin. It will be seen that the time-yield curves are of the same type as those previously obtained at 100° C. Above 100° C. it is difficult to follow the reaction owing to its rapidity and there is evidence of the decomposition

[1] Parts I, II and III, *J. Physical Chem.*, 1935, **39**, 727, 901, 907; Parts IV and V, *Proc. Ind. Acad. Sci.*, (A), 1935, **2**, 483, 605.

TABLE I.

Temperature ° C.	G. benzoin dissolved in 10 g. benzaldehyde
60	2·6
70	4·0
80	5·8
90	8·0
100	10·6

Above 100° C. miscibility is rapidly obtained.

of the benzoin formed by the further action of potassium cyanide. A similar effect was observed by Lachman.[2]

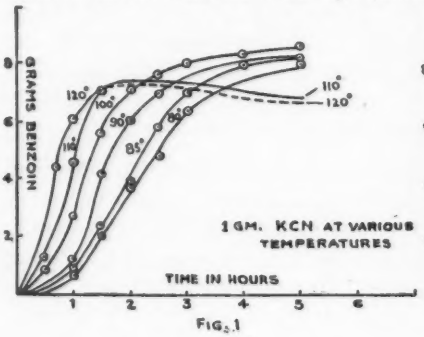

FIG. 1

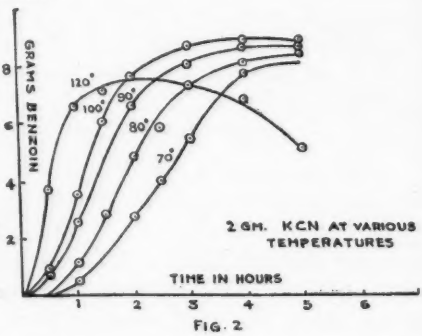

FIG. 2

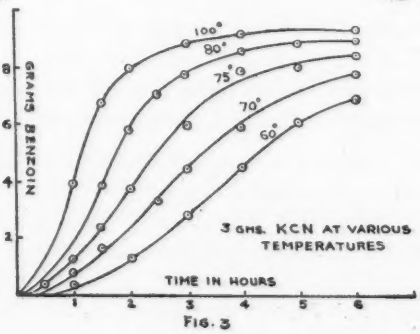

FIG. 3

[2] *J. Amer. Chem. Soc.*, 1924, 46, 710.

A mathematical study of the results shows that the equation which was worked out in Part I for the initial stages of the reaction up to the separation of benzoin can here be applied. The equation is :—

$$t - c' = -1/k_1 [-5/n' + 3 \cdot 45 \log n' - 4 \cdot 60 \log (10 + X' - n')]$$

where n' = g. benzaldehyde remaining at time t,

k_1 = the value of the homogeneous constant,

$X' = 2k'_2/k_1$, k_2' being the heterogeneous constant,

and c' is a constant.

At 100°, k_2' for 1 g. effective KCN per 10 g. benzaldehyde is 0·185, and k_1 is 5·7. Effective KCN, it may be noted, is the gross quantity of KCN used less 0·17 g., since it has been found previously (Part I, p. 730) that 0·17 g. KCN is always ineffective in the experiments. Further experiments have shown that at higher temperatures the inactivity of this small amount of cyanide still persists.

On investigating the application of the above equation, it was found that between 80° C. and 100° C. and possibly up to 120° C., k_1 the homogeneous constant does not change, but retains the value 5·7.

The heterogeneous constant k_2 is found in the range involved to be approximately doubled for each rise in temperature of 10° C. ; this ratio for the temperature coefficient is not unusual. Stern[3] found a similar temperature coefficient for the reaction in aqueous alcoholic solution. We can accordingly write the equation for the temperature range investigated as given above putting k_2 for 1 g. of effective KCN per 10 g. benzaldehyde equal to $0 \cdot 185 \times 2^{\frac{\theta - 100}{10}}$, θ being expressed in ° C.

Table II shows the value of X′ for the various series of experiments made in the present investigation. By choosing suitable values of c' it was found possible to reproduce all the experimental curves obtained between 80° C. and 100° C. up to approximately the point at which from the results given in Table I, benzoin was known to be separating.

At 110° C. and 120° C. there is decomposition of benzoin, but the initial portions of the curves for 1 g. KCN at 110° C. and 120° C. could be reproduced by the same equation. Below 80° C. the regularities in the values of k_1 and k_2' were no longer to be observed ; both appeared to decrease in value with further reduction in temperature.

[3] *Z. physikal. Chem.*, 1905, **50**, 554.

TABLE II.

Temperature ° C.	KCN used (a) g.	KCN effective ($b = a - 0{\cdot}17$) g.	$k_2' = 0{\cdot}185\, b \times 2^{\frac{\theta - 100}{10}}$	$X' = \frac{2k_2'}{5{\cdot}7}$
80	1·0	0·83	0·038	0·013
80	2·0	1·83	0·085	0·030
80	3·0	2·83	0·131	0·046
85	1·0	0·83	0·054	0·019
90	1·0	0·83	0·077	0·027
90	2·0	1·83	0·169	0·059
100	1·0	0·83	0·154	0·054
100	2·0	1·83	0·338	0·119
100	3·0	2·83	0·524	0·184
110	1·0	0·83	0·307	0·108
120	1·0	0·83	0·614	0·216

Summary.

Continuation of the investigation of the benzoin reaction between pure potassium cyanide and pure benzaldehyde in the absence of solvents and diluents has shown that between 80° C. and 110° C. the rate of the fast homogeneous autocatalytic reaction remains unaltered; the slow heterogeneous reaction has its rate approximately doubled for each 10° C. rise in temperature.

DIFFRACTION OF X-RAYS IN ORGANIC GLASSES.

By T. M. K. Nedungadi.

Received August 15, 1938.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

X-Ray diffraction studies with glasses have greatly assisted in elucidating the structure of the amorphous state of matter and its relation to the liquid state. It is well known, even from the early observations of Friedrich[1] on the scattering of X-rays by wax and other amorphous solids and by Jauncey[2] on the scattering by glass, that the diffraction pattern in the case of glasses consists of diffuse haloes as in the case of liquids. This indicates that the arrangement of the molecules or atoms in the glassy state presents a closer analogy to that in the liquid than that in the crystalline state. Later, many inorganic glasses such as vitreous silica, borax glass, etc., have been investigated by workers in the field, notably Randall, Rooksby and Cooper ; Zachariasen ; Wyckoff ; Warren and others,[3] with similar results.

This similarity in the X-ray patterns of the liquid and glass supports the fundamental conception that glass, though it possesses some of the mechanical properties of the solid state, is, nevertheless, to be regarded as an undercooled liquid characterized by optical isotropy and by lack of symmetry or periodicity in the macroscopic arrangement of the structural elements. The transition from the glassy to the liquid state does not take place at a precisely defined temperature and does not involve latent heat effects or any sudden change in the volume as in the case of the transition from the crystalline to the liquid state. Now, it is obvious that the real relation between the liquid and glassy states can only be understood by a detailed study of the changes which take place when an amorphous solid changes to a liquid and *vice versa*. The first attempt to approach the problem from this point of view is that of Dr. Krishnamurthi[4] in his X-ray study of some amorphous solids at the transition temperatures. He has followed up the changes in the diffraction haloes obtained in the case of ordinary rosin, shellac, and of a synthetic resin during the transition from the solid to the liquid state. He noticed that the sharp haloes obtained in the case of the solid became more

diffuse when the substance was melted. Besides, the transition was followed by a contraction in the diameter of the halo in the pattern and an increased scattering at small angles to the primary beam. These observations have been explained by him by means of the theory put forth by Raman and Ramanathan for X-ray diffraction in liquids and amorphous solids. In the light of these facts, some observations of the X-ray diffraction haloes given by liquids which are supercooled and made to pass into the vitreous condition would be of interest in order to further elucidate the nature of the glassy condition and particularly, to determine whether, when the temperature is taken below the softening point, any further rearrangement of molecules takes place. The present work is, hence, an attempt to study simultaneously some organic glasses and their corresponding liquids.

Experimental Technique.

Viscous organic liquids when freed from dust and cooled down to low temperatures are known in many cases to assume the glassy state. In the present investigation, three substances which behave in this manner, namely glycerine, phenyl salicylate and benzophenone have been studied both in the glassy and liquid conditions. The samples were Kahlbaum's purest. Glycerine, which is a liquid at ordinary laboratory temperature, increases in viscosity as it is cooled down and begins to solidify at about 221° K, the temperature T_g[5] at which it becomes a hard glass being 187° K. Phenyl salicylate (Salol) is a solid with the melting point 318° K. If melted and kept undisturbed, it remains a liquid at laboratory temperature 298° K. In order to avoid easy crystallisation, it was found necessary to distil the substance in vacuum. When the pure liquid is cooled, it sets itself as a glass at 238° K. Benzophenone (melting point 322° K) becomes glassy at 219·5° K. Many attempts to keep the two latter substances in the glassy state were unsuccessful, since slight variations of temperature of the glass brought about sudden crystallisation.

For photographing the X-ray diffraction patterns an ordinary flat film camera was used. The experimental arrangement employed in the present investigation was the same as in the powder photograph method of Debye and Scherrer. However, the arrangement had to be modified so that the specimen could be cooled to sufficiently low temperatures. The camera used for the purpose consisted of an air-tight rectangular box (shown in the figure) made of brass and lined inside with lead. The low temperature specimen holder was a copper rod 1·5 cm. in diameter and 10 cm. long, projecting up to about 4 cm. inside the camera through a hole at the bottom fitted with a soft rubber stopper. The liquid was contained in a thin capillary

tube of lead-free glass which by itself did not give any observable diffraction pattern even with very long exposures to X-rays. The capillary tube with the liquid was inserted into a narrow hole which runs down axially to 2 cm. from the end of the copper rod inside the camera. The X-ray beam, collimated by a long fine hole (diameter ·6 mm.) in a lead block, was allowed to traverse the specimen through a small transverse aperture (diameter 3 mm.) which was opened out a little on the film side of the rod, so that the diffracted beam would not strike its edges. The specimen was cooled by keeping the whole length of the copper rod, projecting below the camera, dipped in liquid air. To minimise the effects of conduction from the surrounding air, the part of the rod inside the camera was covered by a thick layer of asbestos, leaving a clear path for the X-ray beam to traverse the specimen.

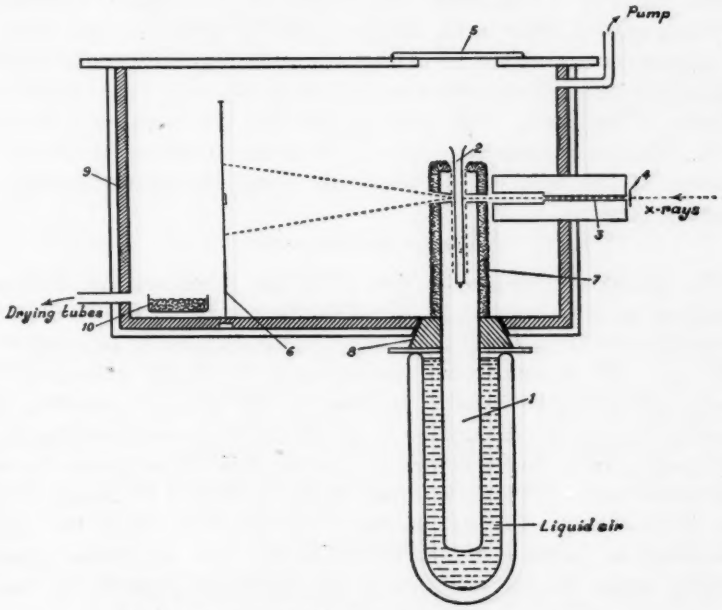

FIG. 1. Schematic Diagram of the X-Ray Camera.

1—Copper Rod; 2—Glass Capillary and the Specimen; 3—Slit; 4—Nickel Foil; 5—Glass Window; 6—Photographic Film; 7—Asbestos Covering; 8—Rubber Stopper; 9—Lead Lining; 10—P_2O_5.

An easy method of avoiding the deposition of ice on the copper rod and the specimen when they were cooled down was to keep the air inside the camera perfectly dry. Hence the camera was covered up with another metal

plate ; the joint between the cover plate and the camera was made air-tight with a putty supplied by Metropolitan Vickers. The camera was evacuated and dry air let in. To remove the water vapour which might still remain in the air, some flat dishes containing phosphorous pentoxide were previously placed inside the camera. The opening of the slit of the camera was closed by a nickel foil (thickness ·06 mm.). This foil, besides making the camera air-tight, also served as the filter for the X-radiation from the copper anti-cathode of the X-ray tube. It was certain that with this arrangement, the copper rod and consequently the specimen attained a temperature sufficiently low, since, on looking through a glass window at the top of the camera, the tendency for the formation of CO_2 flakes on the copper rod was quite visible.

The source of X-rays was a metal Shearer tube, excited by a transformer, the voltage applied being in the neighbourhood of 35 K.V. The nickel filter used completely cuts off the K_β of copper, and the K_α with $\lambda = 1 \cdot 54$ Å (though mixed with a little general radiation) that is transmitted, serves as the monochromatic X-ray beam. The photographic film was kept at a distance of 4·6 cm. from the specimen. With a current of 6 milliamperes in the tube, exposures of the order of 8 hours were found necessary to obtain good diffraction patterns.

Results and Discussion.

The results obtained in the case of all the substances are striking. A comparison of the negatives of the diffraction patterns for the liquid and the glass reveals in the latter (1) a considerable decrease in the scattering at small angles, (2) a conspicuous sharpening of the liquid haloes, and (3) a widening of the liquid haloes. Due to the complicated structure of the molecules, quantitative calculation by the method of Fourier analyses developed by Zernike and Prins[6] was found to be very difficult and hence the results are recorded and explained in terms of the existence of Bragg reflection planes in the liquid. Results obtained from measurements of the negatives are recorded in Tables I, II and III. Column 2 in the tables gives the scattering angle for the direction of the maximum intensity in the halo. The spacings, calculated from the Bragg formula $d = \frac{\lambda}{2 \sin \theta/2}$ where θ is the angle between the direct and the diffracted beams, are given in Column 3. Columns 4 and 5 give the spacings calculated similarly, corresponding to the inner and outer limits to which the halo extends. The last column gives the difference of Columns 4 and 5, and serves to indicate the sharpness of the halo. The photographs are reproduced in Plate II. The observed effects are much more clear in the original negatives than in the prints.

TABLE I.

Glycerine $C_3H_8O_3$. $T_g = 187°$ *K.*

	θ	$d = \frac{\lambda}{2 \sin \theta/2}$ A.U.	Spacing of the inner limit A.U.	Spacing of the outer limit A.U.	Difference in the limits of spacing A.U.
Liquid	19° 34′	4·49	4·91	3·96	·95
Glass	21° 23′	4·14	4·49	3·86	·63

TABLE II.

Phenyl Salicylate $C_{13}H_{10}O_3$. $T_g = 238°$ *K.*

		θ	$d = \frac{\lambda}{2 \sin \theta/2}$ A.U.	Spacing of the inner limit A.U.	Spacing of the outer limit A.U.	Difference in the limits of spacing A.U.
Liquid	1st halo ..	9° 16′	9·53	..	..	..
	2nd „ ..	17° 30′	5·06	5·71	4·63	1·08
	3rd „ ..	..	..	4·63	2·59	2·04
Glass	1st halo ..	10° 10′	8·69	..	..	..
	2nd „ ..	18° 4′	4·95	5·31	4·56	·75
	3rd „ ..	24° 25′	3·64	4·05	2·61	1·44

TABLE III.

Benzophenone $C_{13}H_{10}O$. $T_g = 219°·5$ *K.*

	θ	$d = \frac{\lambda}{2 \sin \theta/2}$ A.U.	Spacing of the inner limit A.U.	Spacing of the outer limit A.U.	Difference in the limits of spacing A.U.
Liquid	18° 54′	4·69	5·23	4·21	1·02
Glass	20° 0′	4·43	4·9	4·16	·74

In the case of liquid glycerine, earlier workers have got one prominent halo with comparatively little scattering at small angles. When the liquid solidifies, this main halo increases in diameter which shows a decrease in the spacing to the extent of ·35 Å. From Column 6 it can be seen that this halo is sharper than that of the liquid. The diffraction pattern for glycerine in the glassy state shows clearly the extent of the decrease in the scattering at small angles.

Liquid salol does not seem to have been investigated by X-rays till now. The liquid pattern consists of three more or less diffuse haloes, the innermost being very faint. The second one is very intense, and the third so faint and diffuse that it is not separated from the second. In the pattern for salol in the glassy state, all the haloes widen out and get so much sharpened that the second and third are well resolved and show themselves up as two separate haloes. Benzophenone gives a pattern similar to that of glycerine, the pattern for the glass showing markedly the widening and sharpening effects.

The above facts can be explained qualitatively by means of our conception of the physical changes taking place when the liquid solidifies to form the glass.

Scattering at Small Angles.—In the particular case where the angle at which X-rays are scattered is very small, the ordinary classical theory of scattering of visible light, developed by Einstein and Smoluchowski for liquids, can be applied with sufficient justification, as was shown by Raman and Ramanathan[7] in their theoretical consideration of the X-ray diffraction in liquids. Now, according to this classical theory of light scattering, the intensity of light scattered due to unit volume of a liquid is proportional to

$$\left(\frac{\mu^2+2}{3}\right)\cdot\frac{n^2RT\beta}{N}$$

where μ is the refractive index of the liquid, n the total number of molecules in the liquid per unit volume, R and N the gas and Avogadro's constants respectively for gm. molecules, and β the isothermal compressibility of the liquid. In the above expression for intensity, both T and β decrease when the substance is cooled down and hence the intensity of scattered light at such small angles should decrease. When the liquid changes into glass, the decrease in compressibility is enormous, β for the hard glass being many times smaller than that for the liquid. Hence the large amount of decrease in the scattering of X-rays that is observed in the case of glasses, is quite consistent with the above considerations.

Sharpening of the Haloes.—The sharpening of the liquid haloes in the glassy state can be considered to be due to the decrease in the fluctuation

of the mean molecular distance in the liquid. On account of the high viscosity of the glass, the molecules get almost fixed up in space and hence, the deviations of the molecular distances from the mean are considerably lessened. The ideal case where there is absolutely no fluctuation in the spacing will be the crystalline state where the diffraction pattern consists of very sharp rings. However, the case of glass is nowhere near that of the crystal, as is evident from the diffuseness of its haloes compared to the sharpness of the rings in the crystal pattern.

Widening of the Haloes.—This is obviously due to a decrease in the mean molecular distance, for, according to the Bragg formula

$$\lambda = 2\, d \sin \theta/2$$

if d decreases, θ the angle at which the maximum scattering occurs increases. This decrease in the value of d in the case of the glass is a consequence of the nearing up of the molecules to form a closer packing in the solid condition.

Now, it is interesting to note that the above results are found to agree with those predicted by Raman and Ramanathan in their consideration of the influence of temperature on the liquid haloes. Their conclusions have been verified in the case of high temperatures by Ramasubramanian[8] and Vaidyanathan.

Thus the above results indicate that when the temperature of the substance is lowered below the softening point, no radical rearrangement of the molecules other than those naturally due to the lowered temperature of the fluid takes place. This idea is supported by observations on light scattering in amorphous solids and undercooled liquids. Experiments on light scattering by glassy salol have shown that the light scattering power in the glassy and liquid states remains of the same order of quantities. Hence the constitution of glass can be considered to be fundamentally the same as that of the liquid, with the difference that in glass, the molecules are nearer each other than those in liquids with almost fixed positions for them, while in the case of liquid their positions are constantly varying.

In conclusion, the author takes this opportunity to record his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., under whose inspiring guidance the present investigation was carried out.

Summary.

Using a modified form of the ordinary X-ray diffraction arrangements, three organic substances, namely glycerine, salol and benzophenone have

been investigated both in the liquid and glassy conditions by means of X-rays. The changes observed in the diffraction patterns when the liquid changes into glass are (1) a large decrease in the scattering at small angles with the primary beam, (2) a considerable sharpening of the haloes, and (3) a widening of the haloes. The first two effects have been explained by taking into consideration the large decrease in the compressibility of the substance as it changes from the liquid to the glassy state and the last one as due to the decrease of the intermolecular distance to form a closer packing of the molecules in the solid condition.

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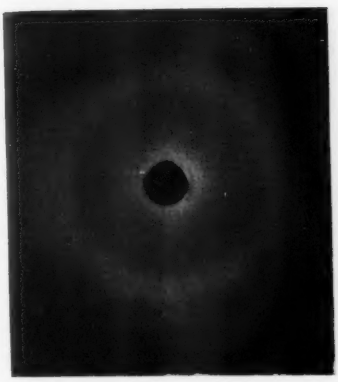
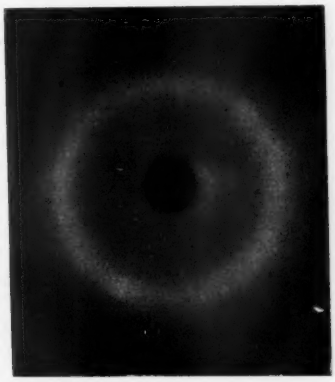
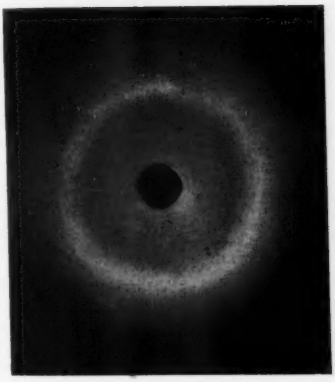
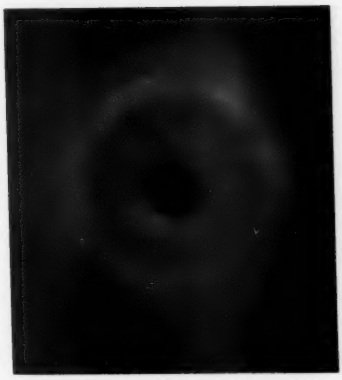
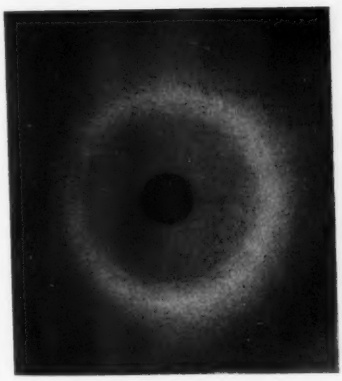
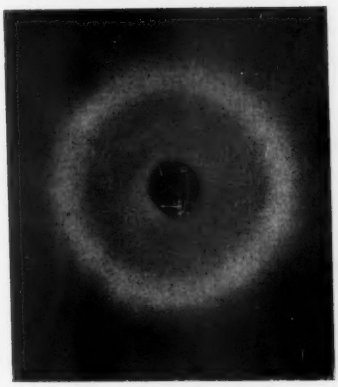



Glycerine

Salol

Benzophenone

Liquid State

Glassy State

RAMAN SPECTRA OF SOME ORGANIC BI-CYCLIC COMPOUNDS.

Naphthalene, Decaline, Tetralin, Indene, *Trans*-β-Decalone, *Trans*-β-Decalol.

By Bishambhar Dayal Saksena.

Received July 22, 1938.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction.*

A knowledge of the complete spectra of molecules along with their polarisation characters is of great importance in the elucidation of their molecular structure. The theory of groups is of great help in this direction. On this theory it is possible to calculate the number and nature of modes of vibration and their selection rules for any molecule possessing some elements of symmetry. According to Wigner[1] the number of oscillations a_p of the type of vibration p, is given by $a_p = \frac{1}{h} \Sigma \chi^{(p)} \epsilon\,(\mathrm{R})$

where $\epsilon\,(\mathrm{R}) = \underset{\text{rotation pure}}{\Sigma\,(u_R - 2)\,(1 + 2\cos\phi)} + \underset{\text{rotation and reflection}}{\Sigma'' u_R\,(2\cos\phi - 1)}$

h is the number of elements of symmetry for a particular group, ϕ the angle of rotation for any particular element of symmetry (axis or plane) which does not alter the character of the group after rotation, u_R the number of points in any symmetry, and $\chi^{(p)}$ is the character of the irreducible representation of various types of elements of the group. Tables for the representation of such characters have been given by Tisza.[2] The number of polarised and depolarised lines for a given molecular structure can thus be found out and compared with the experimental data. The present paper gives the results of an investigation on the Raman spectra and depolarisation measurements of decaline, tetralin, indene, *trans*-β-decalone, *trans*-β-decalol and naphthalene; and these have been discussed in relation to the molecular structure.

2. *Experimental.*

All the substances examined were in the liquid state except *trans*-β-decalol which was a solid. These were purest Kahlbaum's chemicals excepting *trans*-β-decalone and *trans*-β-decalol which were lent to the author by Dr. M. A. G. Rau. These were further purified and twice distilled in vacuum

into a Wood's tube. Two pyrex arcs were used for illumination, and a Hilger Littrow glass spectrograph having a dispersion of 10 A.U. per mm. in the 4358 region was used for photographing the spectra. The plates were measured on a Hilger cross-slide micrometer in comparison with an iron arc spectrum. The accuracy of measurement is about 2 cm.$^{-1}$ for sharp and intense lines.

The depolarisation measurements were made on a Fuess glass spectrograph of high light gathering power. The light from a quartz arc placed at the side was focussed by a glass condenser on the Raman tube which was carefully aligned to the axis of the spectrograph. A quartz double-image prism placed between the slit of the spectrograph and the observation end of the tube separated the scattered radiation into two components, vertical and horizontal, which were focussed by a lens on the slit of the spectrograph. The plate was then run on a microphotometer and the densities of lines in the two components were found out. In cases where the plate showed the background, the density of the line was obtained by subtracting the density of the background from the total density of the line. A set of intensity marks were obtained on the same photographic plate by the method of varying slit widths, using as a source of illumination, a small tungsten filament lamp fed by a current from a freshly charged battery at a constant voltage. Blackening—log I (intensity) curves were drawn for four wave-lengths by running this plate on the microphotometer. All the curves were parallel in their straight portions. The same curves were used for all the plates which were developed in the same strength of the developer for the same time. From the curve corresponding to $\lambda = 4358$, the intensities of the lines in the two components were read off from the known values of their densities and their depolarisation ratios obtained. The ratio determined in this way involves errors due to the spectrograph and other accessories. These were found by taking the spectrum of the direct unpolarised light from the mercury arc after it had passed through a double-image prism, and finding the ratio of intensities in the vertical and horizontal components in the manner stated above. This gave a value of 0·68 for the spectrographic correction. Without altering the experimental arrangements the depolarisation ratios for carbon tetrachloride lines were found and compared with the known values of depolarisation for these lines. Good agreement was observed on making the above correction.

3. Results.

The results of investigation are tabulated in Tables I–VI. The following notation has been used for the assignment of lines :—

$\lambda = 4358 \cdot 34\ e$	$\lambda = 4108\ \ h$	$\lambda = 3663\ o$
$= 4347 \cdot 50\ f$	$= 4077 \cdot 8\ i$	$= 3665\ p$
$= 4339 \cdot 24\ g$	$= 4046 \cdot 5\ k$	$= 3650\ q$
		$= 3906\ m$
		$= 3984\ l$

1. *Decaline.*—The substance has been investigated previously by Bonino and Cella,[3] Mukerji,[4] Jatkar,[5] Mitra,[6] Mutsuno and Han.[7] The following new lines have been observed in the present investigation 740, 970, 1079, 1124, 1451. The lines at 740 and 1144 appear as companions to the intense lines 752 and 1162. The agreement between the results of the previous workers and the author is fairly close. Of the lines recorded 18 are polarised and 19 depolarised.

2. *Tetralin.*—The substance has been investigated by Bonino and Cella,[3] Mukerji,[4] Venkateswaran[8] and Mutsuno and Han.[7] The following new lines have been observed: 788, 1088, 1273, 1293, 1329, 1393, 3036 and 3056. The lines at 1285 and 3049 reported by previous workers are split up into doublets at 1273 and 1293; and 3036 and 3056. The latter may be a combinational frequency given by $3036 = 1604 + 1532$; several doublets are present in the spectra and all the C − H frequencies between 2800 and 3100 excited by $\lambda = 4046$ are resolved into sharp lines, whereas in decaline they appear as broad lines. The wing accompanying the Rayleigh line in tetralin is stronger than in decaline. There are 21 depolarised and 20 polarised lines. The continuous spectrum in tetralin is depolarised.

3. *Indene.*—This has been investigated by Hayashi,[9] Manzoni-Ansidei,[10] and Mutsuno and Han.[7] The author's results agree very closely with those given by Ansidei, but Hayashi's values in general appear to be systematically lower. New frequencies have been observed at 2785, 987, 470 and 320. A great majority of lines show a value of ρ in the neighbourhood of ·50.

4. Trans-*β-Decalone.*—No previous investigation appears to have been made on this compound. It is a substitution product of decaline, two of the H atoms of which are replaced by an O atom in the β-position. The spectrum strongly resembles that of decaline, and has yeilded 39 lines of which 22 are polarised and 15 depolarised.

5. Trans-*β-Decalol.*—The substance was examined in the solid state by the method of complementary filters.[11] In spite of the fact that the substance was purified by repeated crystallisation, it was not possible to get rid of fluorescence. Hence the spectrum is not complete, only 8 lines being observed.

6. *Naphthalene.*—Kahlbaum's pure naphthalene for analysis was distilled in vacuum and sealed in a double walled tube. The outer jacket was filled with water to ensure uniform heating and also to control temperature. As there was only a feeble background, it was possible to determine the depolarisation ratios of Raman lines. The spectrum of naphthalene has been examined by a number of workers—Petrikaln,[12] Kohlrausch and Dadieu[13] (solution), Zimecki[14] (molten), Gockel[15] (molten), Mutsuno and Han[16] (solution), Manzoni[17] (solution), Ananthakrishnan[18] (solid), Canals and P. Pevrot[19] (solid) and Kohlrausch.[20] According to the X-ray evidence,[21] naphthalene possesses a centre of symmetry, and so the vibration spectrum should show only 24 lines. Only 10 lines have been reported for the molten state, 11 for solution, 16 lines for crystal. Pevrot and Canals report 24 lines for the crystal but the assignments are not all correct. One of the lines 702*ff* is in fact *i*-511 and is no new line. In the present case an intense picture was obtained under prolonged exposure and 21 lines were identified. The spectra reported by various workers are given below for comparison.

It may be seen from the table that the lines at 1168 and 1623 appear only in the solid. The line at 1280 in solid is shifted to 1250 in liquid, and two new lines at 191 and 397 are observed in the liquid. Otherwise the spectrum observed by the author contains all the lines reported by one or the other of previous workers.

Molten or solution						Crystal		
Kohlrausch and Dadieu	Zimecki	Gockel	Mutsuno and Han	Manzoni	Author	Ananthakrishnan	Canals and Pevrot	Kohlrausch
Solution	Fusion	Solution	Solution	Molten	Molten	Crystal	Crystal	Crystal
..	..	..	..	..	191 (1)	..	..	..
..	..	..	..	..	397 (1)	..	404 *ff*	..
505 (2)	511 (3)	512 (5)	514 (6)	510 (3)	511 (6)	511 (3)	518 F*f*	513 (6)
..	..	..	..	..	..	..	702 *ff*	..
..	742 (2)	..	..	..	726 (1)	..	743 *ff*	728 (1)
762 (4)	762 (3)	761 (5)	764 (6)	760 (3)	760 (6)	764 (5)	764 F	766 (12)
..	..	778 (1)	..	..	772 (1)	..	..	786 (1)
936 (0)	..	..	..	..	941 (2)	..	..	..
1023 (2)	1026 (3)	1026 (4)	1028 (4)	1023 (3)	1024 (5)	1019 (5)	1018 F	1023 (9)
..	..	..	..	..	..	..	1108 *ff*	..
1142 (0)	..	1153	..	1142 (1)	1142 (2)	1144 (3)	1144 *ff*	1148 (4)
..	..	..	..	..	..	1168 (1)	..	1168 (2)
..	..	..	..	..	1206 (0)	..	1205 *f*	..
1245 (0)	..	1251 (0)	..	1239 (0)	1239 (1)	1240 (2)	1243 *f*	1245 (2)
..	..	..	..	..	1257 (2)	1280 ($\frac{1}{2}$)	1285 *ff*	1280 (2)
..	1323 (0)	1323 (1)	..	1320 ($\frac{1}{2}$)	1326 (1)	1328 (0)	1322 F	1326 (4)

Molten or solution						Crystal		
Kohlrausch and Dadieu	Zimecki	Gockel	Mutsuno and Han	Mauzoni	Author	Ananthakrishnan	Canals and Pevrot	Kohlrausch
Solution	Fusion	Solution	Solution	Molten	Molten	Crystal	Crystal	Crystal
1377 (4)	1377 (0)	1379 (8)	1382 (8)	1377 (8)	1379 (15)	1379 (15)	1381 FF	1384 (20)
1412 (0)	..	..	..	..	1406 (0) ?	..	..	..
..	..	..	..	1433 ($\frac{1}{2}$)	1438 (2)	1440 (1)	1436 *f*F	1446 (2)
..	1460 (4)	1462 (4)	1464 (4)	1462 (3)	1460 (4)	1460 (5)	1462 F	1465 (8)
..	..	..	..	..	1530 (0)	..	..	..
1573 (3)	1575 (4)	1572 (3)	1577 (4)	1576 (3)	1576 (5)	1537 (7)	1576 F	1578 (8)
..	..	..	..	..	..	1623 ($\frac{1}{2}$)	1626 *f*	1628 (1)
..	..	..	..	..	..	..	2980 *ff*	..
..	..	..	..	..	..	3001 (1)	3007 *ff*	..
..	..	..	..	..	..	3025 (1)	3030 *ff*	..
3046 (1)	3058 (4)	3062 (4)	3046 (8)	3064 (8)	3058 (4)	3054 (12)	3058 F	3058 (4)
..	..	..	..	..	3244 (2)	..	3244 F	..

4. Discussion.

For purposes of comparison the spectra of all compounds studied in the present paper are schematically represented in Fig. 1. The frequency shifts of Raman lines are represented horizontally in wave numbers and the intensities are indicated by the heights of the lines. The figure by the side of each line indicates the value of the depolarisation ratio. Depolarised lines are crossed along their entire length. The letters δ (C – H), ν (C – H) C = O, C = C, C – C indicate the types of oscillations.

A general comparison of the spectra reveals the following facts :—

(1) Certain Raman lines have fairly constant frequency shifts and depolarisation ratio in all the compounds. These are joined by dotted lines in the figure. They lie in the regions 400–500 cms.$^{-1}$ and 700–800 cm.$^{-1}$ The ratio of the intensities of these lines as read from the microphotometer curves is 1·03 in naphthalene, 1·10 in decaline and 1·2 in tetralin. The intensity and depolarisation considerations lead us to conlcude that these lines should be ring vibrations of the two fused rings.

(2) Besides the above lines there are two lines in all the compounds, one strong lying in the region 1019–1040, and the other of medium intensity, lying in the region 1075–1090 which change their polarisation characteristics as we pass from compounds containing the two benzene rings to compounds containing two cyclohexane rings. The first line appears polarised (ρ = ·43) in indene, tetralin and naphthalene (ρ = ·55), but is weak and depolarised in decaline and decalone. The other line is polarised in decaline and decalone and tetralin, but unpolarised in others. As benzene and its derivatives show a strong polarised line in the neighbourhood of 1000, while cyclohexane and its derivatives show a depolarised line near 1028, these lines may be expected to come out with the same intensity and polarisation in compounds containing the two fused benzene or cyclohexane rings.

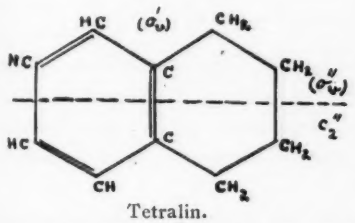
(3) Raman lines having frequency shifts below 200 are present in all the compounds. They are very broad, fairly intense and completely depolarised in tetralin. Such broad low frequecny lines are not generally observed in compounds possessing a single ring-like benzene and its derivatives. Therefore these lines may be attributed to the deformational oscillation of the two rings of these compounds against each other. It may be expected that in molecules possessing a puckered structure their oscillations would be more pronounced and the lines would come out with greater intensity. This may explain the greater intensity of these deformational oscillations in tetralin.

100
500
1000
1500
1800 2700
3000
ν (c⁻¹)
Indene
Naphthalene
Dihydro Naphthalene
Tetralin
Decaline
Trans β Decalone
Trans β Decalol
C≡C
C=O

Fig. 1.

The infra-red spectra of decaline, tetralin and naphthalene have been investigated by Le Comte.[22] The spectra of decalin and naphthalene exhibit greater resemblance than that exhibited by the spectra of benzene and cyclohexane. The infra-red spectra given in Tables VII, VIII and IX show strong absorption bands at 740 and 939 cm.$^{-1}$ which are also exhibited by other compounds containing the naphthalene ring. These lines come out weakly in the Raman spectra.

Tetralin—contains one benzene ring which is plane and one cyclohexane ring which is puckered. Dipole moment[23] measurements indicate a small electrical moment for the molecule. This may be either due to a puckered structure of the molecule or it may be due to a strain in the chemical bonds due to the fusion of the two rings. As the cyclohexane ring is puckered, the first is a likely possibility. Polarisation study of vibration lines in tetralin lends support to this view.



Tetralin.

If we regard all the carbon atoms in tetralin in one plane, the various elements of symmetry are (1) a binary axis C_2'', (2) a plane σ_v'' passing through this axis, (3) a plane σ_h which is the plane of the molecule and an identity E. The symmetry of the group is then C_{2v} which admits of four irreducible representations A_1, A_2, B_1, B_2 which are given below :

Type	Character table				Number of vibrations		Selection rules	
	E	C_2''	σ_h	σ_v''	Ring C_{10}	Molecule $C_{10}H_{12}$	Raman	Infra-red
A_1 ..	1	1	1	1	9	19	pol.	a
A_2 ..	1	1	−1	−1	4	12	dep.	ia
B_1 ..	1	−1	1	−1	8	18	dep.	a
B_2 ..	1	−1	−1	1	3	11	dep.	a
u_R ..	22	0	14	0	for molecule $C_{10}H_{12}$			
ϵ_R ..	60	2	14	0				

The calculation shows that 19 polarised and 41 depolarised lines are to be expected if all the carbon atoms lie in one plane—the plane of molecule σ_h. If, however, the molecule is puckered, the puckering can occur only in the cyclohexane ring, for the benzene ring is known to be plane. Further the

two carbon atoms directly linked to the benzene ring must lie in the plane of the ring, and the two other atoms can lie in the plane of other atoms or displaced from it. In the latter case there will be no axis of symmetry C_2'' but the plane σ_v'' can still exist if both atoms are displaced to one side of the plane σ_h. In this case the group symmetry becomes C_s, the two elements of symmetry being E and σ_v''.

Type	Character table		Number of vibrations		Selection rules	
	E	σ_v''	Ring	Molecule	Raman	Infra-red
A_1	1	1	12	30	pol.	*a*
A_2	1	− 1	12	30	dep.	*a*
u_R	22	0				
ϵ_R	60	0				

The calculation shows that 30 polarised and 30 depolarised lines are to be expected for the given puckered structure. In tetralin, 46 lines have been recorded, of these 20 are polarised and 21 depolarised. The polarisation measurements therefore appear to support the requirements of a puckered structure better than that of a plane.

The infra-red absorption maxima of tetralin are recorded in the following table.

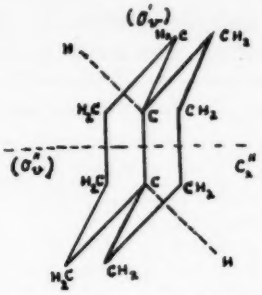
TABLE VII.

Infra-red ..	741 (*s*)		785 (*s*)	806 (*s*)		858	893
Raman	744 (0)		789 (0)	805 (0)	843	868 (0)	904 (0)
Infra-red ..	939 (*s*)		975 (*w*)	1022 (*w*)		1053 (*w*)	
Raman	938 (0)		982 (0)		1037 (*s*)		
Infra-red ..		1100 (*s*)		1227	1266		1429 (*s*)
Raman	1088 (2)		1118 (2)	1234 (0)	1273 (3)		1432 (5)

The coincidence of infra-red and Raman lines shows definitely that the molecule has no centre of symmetry.

Decaline—exists in two isomeric forms as *cis* and *trans*-decaline. The polarisation characteristics of *cis* and *trans*-decalines can be easily calculated on the group theory.

(*a*) Trans-*form*.—The elements of symmetry in this case are (1) a binary axis C_2'', (2) a plane σ_v' perpendicular to the axis and the plane of



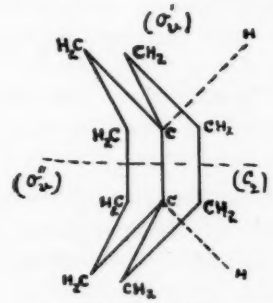
Decaline—*trans*.

paper, (3) a centre of symmetry i and an identity E. The symmetry of the molecule is therefore C_{2h}. The number of vibrations and the character table is given below.

Type	Character table				Number of vibrations		Selection rules	
	E	C_2''	σ_v'	i	Ring C_{10}	Molecule $C_{10}H_{18}$	Raman	Infra-red
A_1	1	1	1	1	7	21	pol.	*ia*
A_2	1	1	−1	−1	6	19	*f*	*a*
B_1	1	−1	1	−1	6	20	*f*	*a*
B_2	1	−1	−1	1	5	18	dep.	*ia*
u_R	28	0	4	0	} for molecule $C_{10}H_{18}$			
ϵ_R	78	2	4	0				

[*f*-forbidden, *ia*-inactive, *a*-active.]

(*b*) Cis-*form*.—The elements of symmetry in this case are (1) a binary axis C_2 perpendicular to the plane of paper and (2) two planes σ_v' and σ_v''



Decaline—*cis*.

passing through this axis and (3) an identity. The symmetry is therefore C_{2v}. The number of vibrations can therefore be written as follows :

Type	Character table				Number of vibrations		Selection rules	
	E	C_2	σ_v'	σ_v''	Ring C_{10}	Molecule $C_{10}H_{18}$	Raman	Infra-red
A_1	1	1	1	1	7	21	pol.	a
A_2	1	1	−1	−1	6	19	dep.	ia
B_1	1	−1	1	−1	6	20	dep.	a
B_2	1	−1	−1	1	5	18	dep.	a
u_R	28	0	4	0	} for molecule $C_{10}H_{18}$			
ϵ_R	78	2	4	0				

These calculations show that 21 polarised and 57 depolarised lines are to be expected in the spectrum of *cis*-decaline while 21 polarised and 18 depolarised lines are to be expected in the spectrum of *trans*-decaline.

To verify these numbers it is necessary to get *cis* and *trans* spectra separately. In the present investigation the decaline used is a mixture of *cis* and *trans* molecules, the *trans*-form predominating. The spectrum of decaline shows a number of pairs of fine lines, one in each pair can be assigned to the *cis*- and the other to the *trans*-form. The detection of such lines has been facilitated by the use of a high dispersion spectrograph. Such pairs are to be expected in the spectra of mixtures of *cis* and *trans* isomers, because, as the structures of the two forms are not very different, the frequency differences between the vibration lines of the two forms cannot be expected to be large. In order to assign the lines to the *cis*- and *trans*-forms, the following procedure was adopted. A comparison was first made with the spectrum of *trans*-β-decalone which is completely *trans*, and *trans* lines isolated. These are then compared with the infra-red spectrum of decaline as reported by Le Comte. The infra-red lines for the *trans*-form of decaline are forbidden in Raman effect, and therefore the infra-red lines which are present as Raman lines should belong to the *cis*-form of decaline. The infra-red spectrum of decaline is given in Table VIII.

It appears that the strong sharp line at 741 is the symmetric oscillation of the *cis*-form whereas 751 is the symmetric oscillation of the *trans*-form. Barring the lines 785, 835, 917, 1414, all the others may be taken as representative of the *cis*-form.

TABLE VIII.

Infra-red ..	741 (*s*)	798 (*w*)	835 (*w*)		917 (*w*)		939 (*s*)
Raman	740 (3)	798 (1)					932 (0)
Infra-red ..	1022 (0)	1220 (*w*)		1299 (*w*)		1414 (*w*)	
Raman	1018 (0)	1233 (0)		1273 (2)			

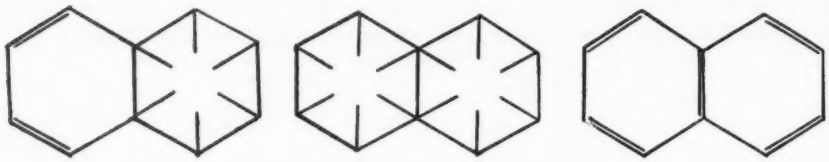
The following lines may thus be assigned to *cis*- and *trans*-forms :

Cis-form			*Trans*-form		
Jatkar	Author		Jatkar	Author	
	$\Delta\nu$	ρ		$\Delta\nu$	ρ
	329 (0)	D		180 (0)	D
539 (0)				406 (5)	·7
595 (3)	595 (3)	·53		446 (1)	P
	740 (3)	·46	491 (5)	491 (5)	·45
794 (1)	798 (0)	D		547 (0)	D
	932 (0)	D		751 (3)	·45
	1018 (1)	D		848 (4)	·47
1040 (2)	1046 (2)	D	881 (3)	875 (2)	·70
	1088 (1)	P	957 (1)	970 (0)	D
	1124 (2)	P	996 (2)	988 (1)	D
	1162 (2)	D		1056 (2)	D
	1134 (0)	D		1079 (2)	P
	1233 (0)	D	1145 (3)	1144 (1)	D
1270 (5)	1273 (2)	D	1234 (1)	1242 (0)	D
1347 (3)	1348 (6)	D		1254 (0)	D
			1363 (5)	1358 (5)	·8
				1444 (6)	·8

The results of the author agree with those of Jatkar,[5] who worked with a concentrated form of *trans*-decaline. If we take the region 0 — 1200 as belonging to the carbon ring we find 5 polarised and 7 depolarised lines which show good agreement with the calculated number of 7 polarised and 5

depolarised lines. In the *cis*-form we find 8 polarised and 15 depolarised lines which agree with the calculated number of 7 polarised and 17 depolarised lines.

Naphthalene.—The molecule of naphthalene contains two fused benzene rings, but on account of the different chemical behaviour of the two rings, three different types of structural formulæ have been proposed for the



1 2 3

Structural formulæ of naphthalene molecule.
1. Willstätter and Wäser. 2. Bamberger. 3. Erlenmeyer.

molecule, *viz.*, those of Erlenmeyer, Bamberger[24] and Wilstätter and Wäser[25] The first two, marked 3 and 2, have a symmetry D_{2h}, the elements of symmetry being the three binary axes C_2'', C_2', and C_2; the three planes of symmetry, σ_v'', σ_v', σ_h the last named being the plane of molecule; and a centre of symmetry i, and an identity. The following tables give the character table as well as the number of vibrations for symmetry D_{2h}. There are 8 modes of irreducible representation.

Type	Character table								Number of vibrations		Selection rules	
	E	C_2	$C_2{}^1$	C_2''	i	σh	$\sigma' v$	$\sigma v''$	Ring C_{10}	Raman	Raman	Infra
A_1	1	1	1	1	1	1	1	1	5	9	pol.	*ia*
A_2	1	1	−1	−1	1	1	−1	−1	4	8	dep.	*ia*
B_1	1	−1	1	−1	1	−1	1	−1	1	3	dep.	*ia*
B_2	1	−1	−1	1	1	−1	−1	1	2	4	dep.	*ia*
A_1'	1	1	1	1	−1	−1	−1	−1	2	4	*f*	*f*
A_2''	1	1	−1	−1	−1	−1	1	1	2	4	*f*	*a*
B_1'	1	−1	1	−1	−1	1	1	−1	4	8	*f*	*a*
$B_2{}^1$	1	−1	−1	1	−1	1	−1	1	4	8	*f*	*a*
u_R	18	0	2	0	0	18	2	0				
ϵ_R	48	2	0	2	0	18	2	0				

In the third case the symmetry is C_{2v}, the elements of symmetry being C_2'' (binary axis), σ_v'' the plane passing through this axis, and σ_h the plane of the molecule. The number of vibrations is given in the following table.

Type	Character table				Number of vibrations		Selection rules	
	E	C_2''	σ_h	σ_v''	Ring C_{10}	Molecule $C_{10}H_8$	Raman	Infra-red
A_1	1	1	1	1	9	17	pol.	a
A_2	1	1	−1	−1	4	8	dep.	ia
B_1	1	−1	1	−1	8	14	dep.	a
B_2	1	−1	−1	1	3	9	dep.	a
u_R	18	0	18	0	} for molecule $C_{10}H_8$			
ϵ_R	48	2	18	0				

Kohlrausch[26] and Bonino[27] have also discussed the symmetry of the naphthalene molecule. According to the above calculation we should expect 9 polarised and 15 depolarised lines for the molecule for symmetry D_{2h} and 17 polarised and 31 depolarised lines for symmetry C_{2v}. In the present investigation 21 lines have been observed of which 9 are polarised and 12 depolarised. In the region 0—1200 belonging to the ring, we find 5 polarised and 5 depolarised lines, the number calculated for symmetry D_{2h} being 5 polarised and 7 depolarised lines. Further in the infra-red 17 lines out of 20 expected lines have been observed. All the above facts are fully in agreement with the symmetry D_{2h} of the naphthalene molecule. In this symmetry, the molecule has a centre of symmetry and, therefore, the frequencies corresponding to infra-red absorption are forbidden in Raman effect. Infra-red spectra of naphthalene have been investigated by Stang[28] and Le Comte.[29] The infra-red and Raman lines and their polarisation characters are shown in Table IX.

It is clear from the table that the positions of infra-red and Raman lines do not coincide, which fact is in accordance with symmetry D_{2h}. The polarisation values of naphthalene lines such as 511, 764, 1024 are quite in agreement with the values found for these lines in other substances. The line 1379 is very strong and highly polarised and so appears to be a breathing frequency of the molecule.

TABLE IX.

Raman ..	3244 D	3058 P	..	..	..	..	..	..	1576 D
Infra-red ..	..	..	3030	..	2380	1940	1724	1584	..
Raman ..	1530 D	..	1460 P	1438 D	1406 D	..	1378 P	1326 P	..
Infra-red ..	..	1492	..	..	..	1389	..	..	1275
Raman ..	1239 D	..	1205 D	1142 D	..	1024 P	..	..	941 P
Infra-red ..	..	1220	..	..	1125	..	1000	961	..
Raman ..	..	..	..	772 P	760 P	728 D	..	..	511 P
Infra-red ..	881	820	782	..	..	..	714	623	..
Raman ..	397 D	191 D							

Indene.—Indene contains one benzene and one pentadiene ring. The spectrum of indene closely resembles that of dihydronaphthalene. The molecule is very unsymmetric, and so nothing can be inferred from polarisation data.

Trans-*β-decalone.*—The spectrum of this substance agrees with that of decaline, but all the frequencies are in general lowered. However, there are some striking differences in the spectra of the two substances. The line at 375 which is weak and depolarised in decaline appears strong and polarised in decalone; and the strong line at 491 in decaline is replaced by two weak lines one polarised and another depolarised in decalone. The δ (C—H) vibration in decalone shows three shifts 1417, 1441, 1447 which agree with those observed in cyclohexanone in the same region. The C = O shift in decalone has the same shift and depolarisation as in cyclohexanone.

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Summary.

The Raman spectra of naphthalene, decaline, tetralin, indene, *trans-β*-decalone and *trans-β*-decalol have been studied, the last two for the first time. Polarisation measurements have also been made in the case of all these compounds excepting *trans-β*-decalol. The molecular structures of decaline, tetralin and naphthalene have been studied in the light of polarisation data and the symmetries of the molecules. The results indicate a puckered structure for tetralin, and a centro-symmetric structure for naphthalene. In decaline the *cis* and *trans* lines have been separated; the observed polarisation characteristics of these forms agree with the group theory results.

The determination of the values of ρ for all these substances has been made for the first time, and the results are given in Tables I–VI.

TABLE I.

Decaline.

No.	λ	$\tilde{\nu}$	I	Assignment	No.	λ	$\tilde{\nu}$	I	Assignment
1	4998·126	20002	1	*e*–2936	25	4525·93	22089	5 *s*	*e*–849
2	4994·016	20018	2	*e*–2920	26	4514·90	22142	1 *s*	*e*–796 } *f*–849 }
3	4978·48	20083	2	*e*–2855	27	4505·85	22187	5 *s*	*e*–751
4	4651·19	21495	6 *b*	*e*–1443 }	28	4503·83	22197	5 *s*	*e*–741
		21503	0	*e*–1451 }					
5	4638·02	21555	0	*f*–1443	29	4492·0	22255	1	*e*–683 } *f*–741 }
6	4632·73	21579	2 *d*	*e*–1359	30	4474·45	22343	5	*e*–595
7	4630·27	21591	3 *d*	*e*–1347	31	4464·10	22395	1	*e*–543 } *f*–595 }
8	4620·0	21639	0	*f*–1355					
9	4612·45	21664	2 *s*	*e*–1274	32	4453·69	22447	6	*e*–491
10	4610·49	21684	2 *s*	*e*–1254	33	4444·70	22492	1	*e*–446 } *f*–491 }
11	4608·13	21695	0	*e*–1243	34	4436·8	22532	6	*e*–406
12	4605·59	21707	0	*e*–1231	35	4430·85	22563	1	*e*–375
13	4591·55	21773	10 *d b*	*e*–1165 } *k*–2932 }	36	4425·64	22589	1	*e*–349
14	4587·44	21793	10 *d*	*e*–1145 } *k*–2912 }	37	4416·0	22644	0	*m*–2948 } *e*–294 }
					38	4393·2	22757	0	*e*–180
15	4582·76	21815	2	*e*–1125 } *k*–2890 }	39	4387·6	22785	0	*e*–153
16	4575·48	21850	(1)	*e*–1088 } *f*–1145 }	40	4298·14	23259	6	*k*–1446
					41	4282·41	23345	3	*k*–1360
17	4573·71	21858	10 *b*	*e*–1080 } *k*–2847 }	42	4280·57	23355	1	*k*–1350
18	4568·66	21882	2 *s*	*e*–1056	43	4266·34	23433	2	*k*–1272
19	4566·60	21892	2 *s*	*e*–1046	44	4262·98	23451	2	*k*–1254
20	4567·11	21923	1 *b*	*e*–1015	45	4260·95	23463	1	*k*–1242
21	4553·89	21951	1	*e*–987	46	4258·88	23473	1	*k*–1232
22	4542·50	22008	0	*e*–930	47	4245·93	23545	2	*k*–1160
23	4533·81	22050	1	*k*–2655	48	4242·89	23562	1	*k*–1143
24	4531·4	22062	1	*e*–876	49	4239·5	23581	0	*k*–1124

TABLE I—(*Contd.*).

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
50	4232·86	23618	0	*k*–1087	64	4146·64	24109	5	*k*–596
51	4231·24	23627	0	*k*–1078	65	4139·05	24154	0	*k*–551
52	4227·44	23648	4 *s*	*k*–1057	66	4128·80	24213	6	*k*–492
53	4225·59	23658	4 *s*	*k*–1047 } *i*–849 }	67	4114·21	24299	6	*k*–406
					68	4109·80	24325	0	*k*–375
54	4219·34	23694	1 *d*	*k*–1011	69	4104·10	24359	2 band	*k*–346 *o*–2936
55	4215·28	23716	1 *b*	*k*–989					
56	4211·44	23738	1 *b*	*k*–967	70	4101·69	24374	2 band and line	*k*–331 *o* 2920
57	4206·9	23770	0	*k*–935					
58	4194·83	23832	1	*k*–873	71	4092·86	24415	4 (*b*)	*k*–290 *p*–2938
59	4190·49	23857	5	*k*–848	72	4091·58	24433	4 *bd*	*q*–2929 *o*–2855
60	4181·70	23907	0	*k*–798 } *i*–595 }	73	4087·93	24455	4 *bd*	*q*–2936
61	4173·6	23953	5	*k*–752	74	4085·30	24471	4 *bd*	*p*–2988 } *q*–2920 }
62	4171·67	23965	3	*k*–740					
63	4162·20	24019	0	*k*–686 } *i*–491 }	75	4074·8	24534	4 *bd*	*q*–2854

$\overline{\Delta\nu}$	150 (0)	180 (0)	294 (0) ?	329 (0)	347 (0)	375 (1)	406 (5)
ρ	..	D	P	D	D	D	·69
$\overline{\Delta\nu}$	446 (1)	491 (5)	547 (0)	595 (3)	684 (0) ?	740 (3)	751 (3)
ρ	P	·43	D	·49	P ?	·46	·46
$\overline{\Delta\nu}$	798 (1)	848 (4)	875 (2)	930 (0)	970 (1)	988 (1)	1012 (0)
ρ	P	·46	D	D ?	D	·70	D
$\overline{\Delta\nu}$	1046 (2)	1056 (2)	1079 (1)	1088 (1)	1124 (2)	1144 (0)	1162 (2)
ρ	·75	·75 ?	P	P	P	D	D
$\overline{\Delta\nu}$	1234 (0)	1242 (0)	1254 (2)	1273 (2)	1348 (5)	1359 (5)	1444 (6)
ρ	D	D ?	·80	·80	·70	·70	·75

$\overline{\Delta\nu}$	1451 (0)	2655 (1)	2855 (8)	2890 (0)	2920 (8) 2936 (8)
ρ	D	..	·45	..	·45 ·52

TABLE II.

Tetralin.

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
1	5028·3	19882	1	*e*–3056	26	4578·22	21794	3	*f*–1201 } *k*–2919 }
2	5023·2	19902	1	*e*–3036	27	4581·52	21821	3 *s*	*e*–1117
3	5017·5	19925	1	*e*–3013	28	4577·55	21839	2	*k*–2866
4	4999·6	19996	2	*e*–2942	29	4575·99	21847	2 *s*	*e*–1091
5	4993·9	20019	1	*e*–2919	30	4571·81	21867	5	*e*–1071 } *k*–2838 }
6	4984·6	20033	0	*e*–2905	31	4564·82	21900	10	*e*–1038
7	4979·7	20076	1	*e*–2862	32	4556·13	21942	0	*e*–996
8	4972·8	20104	0	*e*–2834	33	4554·17	21952	1	*e*–986 } *f*–1038 }
9	4686·0	21334	6 *s*	*e*–1604	34	4543·31	22004	1	*e*–934 } *g*–1038 }
10	4680·6	21359	2 *s*	*e*–1579	35	4536·64	22036	0	*e*–902
11	4668·9	21393	1	*f*–1602	36	4529·62	22071	0	*e*–867
12	4663·3	21438	0	*e*–1500	37	4519·77	22119	1	*e*–819
13	4652·1	21489	1	*e*–1449	38	4517·26	22131	1	*e*–807
14	4648·6	21506	5	*e*–1432 } *i*–3010 }	39	4513·95	22147	0	*e*–789
15	4640·5	21543	0	*e*–1395	40	4508·08	22176	0	*e*–762
16	4636·8	21560	2	*e*–1378 } *f*–1435 }	41	4504·12	22196	0	*e*–742
17	4630·99	21596	2	*e*–1342 } *i*–2919 }	42	4500·63	22213	10 *s*	*e*–725
18	4628·36	21610	1 *s*	*e*–1328	43	4496·02	22236	0	*e*–702
19	4622·32	21628	2 *s*	*e*–1310	44	4489·64	22267	1	*f*–725
20	4618·50	21646	4 *s*	*e*–1292 } *k*–3057 }	45	4483·00	22300	0	*g*–725
21	4614·31	21666	2 *s*	*e*–1272 } *k*–3034 }	46	4471·57	22357	5	*e*–581
22	4608·22	21694	0	*e*–1248	47	4465·72	22386	0	*e*–552
23	4606·65	21702	0	*e*–1236	48	4456·14	22435	2	*e*–503
24	4599·06	21737	6	*e*–1201	49	4446–32	22484	1	*e*–454
25	4592·65	21768	5	*e*–1170 } *k*–2937 }	50	4441·85	22507	4	*e*–431
					51	4432·0	22537	00	*m*–3036

TABLE II—(*Contd.*).

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
52	4435·5	22547	00	*m*–3056	80	4218·95	23700	0	*k*–1005
53	4414·52	22646	0	*e*–292 } *m*–2946 }	81	4214·52	23721	0	*k*–984
54	4408·76	22676	5	*e*–262	82	4205·50	23772	0	*k*–934
55	4389·00	22778	8	*e*–160	83	4201·81	23792	0	*k*–913
56	4382·74	22816	3	*e*–122	84	4191·06	23842	1	*k*–863
57	4367·58	22882	3	*g*–157	85	4184·89	23889	1	*k*–826
58	4352·74	23096	2	*e*–$\overline{158}$	86	4182·76	23901	0	*k*–804
59	4327·52	23101	8	*k*–1604	87	4180·01	23917	0	*k*–788
60	4323·15	23125	3	*k*–1580	88	4175·42	23943	0	*k*–762
61	4308·86	23201	1	*k*–1504	89	4171·59	23965	0	*k*–742
62	4307·20	23210	0	*i*–1307	90	4168·62	23982	10	*k*–725
63	4300·9	23244	0	*i*–1272	91	4164·42	24006	1	*k*–701
64	4298·37	23258	1	*k*–1447	92	4143·43	24127	4	*k*–580
65	4295·58	23273	5	*k*–1432	93	4140·18	24147	0	*k*–554
66	4287·97	23314	0	*k*–1391	94	4130·58	24203	2	*k*–502
67	4285·82	23326	1	*k*–1379	95	4128·77	24213	0	*k*–492
68	4281·16	23358	1	*k*–1347	96	4126·30	24228	0	*k*–477
69	4278·10	23375	2	*k*–1330 } *e*–437 }	97	4122·97	24247	3	*k*–458
70	4270·22	23411	1	*k*–1294	98	4118·38	24276	3	*k*–429
71	4266·67	23431	0	*k*–1274	99	4115·06	24296	0	*k*–409 } *p*–3057 }
72	4260·48	23469	0	*k*–1236	100	4111·99	24312	2	*k*–393
73	4257·80	23480	0	*i*–1036	101	4108·12	24335	2	*p*–3018 } *q*–3053 }
74	4253·29	23504	6	*k*–1201	102	4106·15	24347	2	*i*–162 } *q*–3041 }
75	4245·73	23546	(1)	*k*–1159	103	4103·87	24367	2	*o*–2919
76	4237·35	23593	0	*k*–1112					
77	4232·0	23619	0	*k*–1086	104	4095·08	24413	3	*k*–292 } *p*–2940 }
78	4229·19	23639	1	*k*–1066	105	4089·1	24448	4	*k*–257 } *p*–2905 }
79	4223·95	23668	10	*k*–1037 } *e*–730 }					

TABLE II—(*Contd.*).

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
106	4086·56	24463	1	*o*–2830 } *q*–2919 }	108	4066·5	24584	2	*k*–121
107	4070·5	24547	3	*k*–158	109	4026·1	24831	0	*k*–$\overline{121}$

$\overline{\Delta\nu}$	121 (3)	160 (8)	260 (5)	430 (4)	456 (1)	503 (2)	553 (0)	580 (4)
ρ	D	·80	·74	·70	D	P	P	·67
$\overline{\Delta\nu}$	701 (0)	725 (10)	742 (0)	762 (0)	789 (0)	805 (0)	819 (2)	865 (1)
ρ	P	·51	D	P	P	D ?	D	D
$\overline{\Delta\nu}$	902 (2)	934 (1)	988 (1)	1037 (10)	1068 (2)	1088 (1)	1117 (1)	
ρ	P	P	D	·46	D	P ?	P	
$\overline{\Delta\nu}$	1165 (2)	1201 (6)	1236 (0)	1273 (1)	1293 (2)	1310 (1)	1328 (1)	
ρ	D	·48	D	D	·61	..	P	
$\overline{\Delta\nu}$	1342 (2)	1381 (2)	1393 (0)	1432 (5)	1448 (2)	1502 (0)	1579 (2)	
ρ	P	P	..	·80	D	D	D	
$\overline{\Delta\nu}$	1604 (4)	2836 (3)	2862 (3)	2905 (2)	2919 (4)	2942 (6)		
ρ	·81	P	P	..	D	·71		
$\overline{\Delta\nu}$	3013 (1)	3036 (4)	3056 (4)					
ρ	..	P	P					

TABLE III.

Indene.

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
1	5043·0	19824	0	*e*–3114	26	4547·1	21973	1	*e*–965 } *f*–1022 }
2	5032·2	19863	1	*e*–3075					
3	5028·0	19883	1	*e*–3055	27	4545·54	21993	3 *s*	*e*–945
4	4993·6	20028	(0)	*e*–2910	28	4541·04	22016	1	*e*–922
5	4988·6	20048	1	*e*–2890	29	4528·61	22076	2 *s*	*e*–862
6	4960·6	20153	0	*e*–2785	30	4522·11	22107	3 *s*	*e*–831
7	4687·3	21328	10 *s*	*e*–1610	31	4514·07	22147	0	*f*–860
8	4682·9	21348	3 *s*	*e*–1590	32	4508·76	22173	1	*e*–765 } *f*–831 }
9	4674·8	21385	10 *br*	*e*–1553 } *f*–1610 }	33	4501·66	22208	6 *s*	*e*–730
10	4662·6	21442	3	*e*–1496 } *f*–1553 }	34	4512·6	22263	1	*e*–675 } *f*–732 }
11	4654·02	21482	6	*e*–1456	35	4473·61	22347	5	*e*–591
12	4640·7	21542	3	*e*–1396 } *f*–1453 }	36	4461·96	22405	5 *s*	*e*–533 } *f*–590 }
13	4633·2	21577	6 *s*	*e*–1361	37	4454·4	22443	0	*e*–490
14	4628·97	21602	1	*e*–1336	38	4449·9	22465	(1)	*f*–533 } *e*–473 }
15	4622·03	21630	4 *db*	*f*–1365 } *e*–1308 } *k*–3075 }	39	4440·0	22516	1	*e*–422
					40	4431·85	22557	2	*e*–381
16	4618·1	21648	3 *br*	*e*–1290 } *k*–3057 }	41	4420·0	22618	1	*e*–320
17	4615·39	21661	4 *bd*	*e*–1277 } *k*–3044 }	42	4408·3	22678	0	*m*–2914
18	4604·8	21710	3 *s*	*e*–1227	43	4397·2	22735	3	*e*–203
19	4600·22	21732	6	*e*–1206	44	4388·57	22790	0	*f*–205
20	4587·87	21790	1	*e*–1148 } *f*–1206 }	45	4328·35	23097	6	*k*–1608
					46	4324·82	23116	2	*k*–1589
21	4582·47	21816	2	*k*–2890	47	4317·72	23154	6	*k*–1551
22	4579·96	21831	4 *d*	*e*–1107	48	4307·0	23211	0	*k*–1494
23	4571·94	21866	4 *s*	*e*–1072	49	4300·19	23248	4	*k*–1457
24	4561·33	21917	6 *s*	*e*–1021	50	4288·28	23313	4	*k*–1392
25	4554·50	21950	(00)	*e*–988	51	4282·4	23345	4	*k*–1360

TABLE III—(*Contd.*).

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
52	4272·5	23398	1	*k*–1307	67	4175·67	23942	0	*k*–763
53	4269·0	23418	(0)	*k*–1287	68	4173·60	23953	0	*k*–752
54	4267·0	23429	1	*k*–1276	69	4169·66	23976	6	*k*–729
55	4257·68	23480	2	*k*–1225	70	4145·87	24114	3	*k*–591
56	4253·80	23502	6 *s*	*k*–1203	71	4141·0	24142	(0)	*e*–$\overline{1204}$
57	4245·0	23555	0	*k*–1150	72	4135·54	24174	3	*k*–531 } *o*–3075 }
58	4237·63	23599	3	*k*–1106*	73	4128·0	24218	1	*k*–487
59	4229·41	23637	(2)	*k*–1068*	74	4125·64	24243	1	*k*–467
60	4220·62	23687	(4)	*k*–1018	75	4117·57	24279	2	*k*–426 } *p*–3075 }
61	4215·2	23718	(0)	*k*–987	76	4110·44	24322	2 *d*	*k*–383 } *p*–3037 }
62	4211·5	23738	(0)	*k*–967	77	4100·7	24379	2 *d*	*k*–326
63	4207·6	23760	(2) *d*	*k*–945	78	4095·98	24407	2 *d*	*o*–2885
64	4203·0	23786	2 *d*	*k*–919	79	4090·41	24441	2 band	*k*–264 } *q*–2940 ? }
65	4192·58	23845	1	*k*–860					
66	4187·56	23874	3	*k*–831*					

* Shows a doublet structure in the lines.

$\overline{\Delta\nu}$	203 (3)	320 (0)	381 (2)	422 (1)	470 (0)	489 (0)	532 (5)
ρ	·67	..	·69	P	..	..	·69
$\overline{\Delta\nu}$	591 (5)	675 (0)	729 (6)	764 (1)	831 (3)	861 (2)	931 (1)
ρ	·75	..	·51	D	·59	D	P
$\overline{\Delta\nu}$	945 (2)	965 (0)	987 (0)	1019 (6)	1070 (4)	1106 (4)	
ρ	·69	..	..	·45	·61	·70	
$\overline{\Delta\nu}$	1204 (8)	1227 (3)	1276 (2)	1288 (1)	1307 (1)	1336 (1)	
ρ	·59	D	·59	P	D	D	
$\overline{\Delta\nu}$	1360 (6)	1394 (3)	1456 (6)	1495 (0)	1552 (8)	1589 (2)	
ρ	·68	D	·68	..	·62	D	
$\Delta\nu$	1609 (8)	2785 (1)	2890 (2)	2910 (3)	3055 (3)	3075 (1)	3114 (1)
ρ	·68	..	·65	·66	·60	..	..

TABLE IV.

Trans-*β*-*Decalone*.

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
1	4998·5	19990	6 *br*	*e*–2948	29	4492·10	22255	1	*f*–739 ⟩ *e*–683 ⟩
2	4994·29	20011	2	*e*–2927	30	4466·0	22385	1	*e*–553
3	4974·84	20095	6 *br*	*e*–2842	31	4458·5	22423	1	*e*–515
4	4710·62	21228	4 *br*	*e*–1710	32	4452·83	22452	2	*e*–486
5	4680·10	21361	(00)	*e*–1577 ?	33	4443·10	22500	0	*e*–438
6	4652·01	21490	(1)	*e*–1448	34	4435·21	22541	2	*e*–397
7	4650·43	21497	4 *or*	*e*–1441	35	4429·91	22567	4	*e*–371
8	4645·10	21522	0	*e*–1416	36	4418·70	22625	0	*f*–371
9	4638·00	21552	0	*e*–1386	37	4409·9	22670	1	*e*–268 ⟩ *m*–2927 ⟩
10	4634·34	21574	5	*e*–1364 ⟩ *i*–2948 ⟩	38	4402·7	22707	0	*e*–231 ?
11	4624·50	21618	0	*e*–1320	39	4393·0	22757	1	*e*–181
12	4619·29	21640	0	*f*–1359	40	4383·5	22807	0	*i*–1709
13	4609·65	21688	4 *br*	*e*–1250	41	4325·0	23115	0	*k*–1585
14	4602·94	21719	2	*e*–1219	42	4298·2	23269	1	*k*–1446
15	4594·07	21761	8 *bd*	*e*–1177 ⟩ *k*–2944 ⟩	43	4297·07	23265	2	*k*–1440
16	4591·73	21772	4	*e*–1166 ⟩ *k*–2933 ⟩	44	4293·0	23287	0	*k*–1418
17	4584·27	21808	6	*e*–1130	45	4287·3	23318	0	*k*–1387
18	4572·47	21864	8 *br*	*e*–1071 ⟩ *k*–2841 ⟩	46	4282·69	23345	4	*k*–1360
19	4567·92	21886	1	*e*–1052	47	4274·5	23388	0	*k*–1317
20	4563·48	21907	0	*e*–1031	48	4262·29	23455	4	*k*–1250
21	4550·58	21969	1	*e*–969	49	4256·06	23489	1	*k*–1216
22	4546·50	21989	0	*e*–949	50	4249·60	23525	1	*k*–1180
23	4539·20	22024	1	*e*–914	51	4247·4	23537	1	*k*–1168
24	4527·65	22080	1	*e*–858	52	4240·49	23576	4	*k*–1129
25	4523·31	22102	1	*e*–836	53	4229·57	23636	2	*k*–1069
26	4514·60	22144	0	*e*–794	54	4225·95	23655	2	*k*–1050
27	4510·6	22164	1	*e*–770	55	4222·03	23679	0	*k*–1026
28	4503·54	22199	6	*e*–739	56	4278·4	23699	0	*h*–739

TABLE IV—(*Contd.*).

No.	λ	$\tilde{\nu}$	I	Assignment	No.	λ	$\tilde{\nu}$	I	Assignment
57	4211·42	23738	1	*k*–967	67	4132·06	24194	1	*k*–515
58	4207·90	23758	1	*k*–947	68	4127·05	24224	1	*k*–481
59	4203·8	23781	0	*k*–916	69	4119·55	24269	0	*k*–436
60	4191·44	23851	1	*k*–854	70	4112·58	24310	2	*k*–395
61	4188·45	23870	1	*k*–835	71	4109·8	24330	4 *br*	*k*–373 / *o*–2962
62	4180·50	23914	0	*k*–791	72	4092·0	24431	10 *br*	*k*–274 / *p*–2923
63	4176·91	23934	1	*k*–771					
64	4171·41	23965	4	*k*–740	73	4085·7	24460	10 band	*k*–237 / *q*–2920
65	4143·42	24128	0	*k*–677	74	4077·8	24521	8 *br*	*k*–184 / *p*–2842
66	4139·30	24152	1	*k*–553					

[br = broad; bd = broad and diffuse.]

$\overline{\Delta\nu}$	182 (1)	270 (1)	372 (4)	396 (2)	437 (0)	483 (2)	515 (2)
ρ	·54	P	·56	·62	P	·45	·55
$\overline{\Delta\nu}$	553 (1)	660 (1)	739 (6)	770 (0)	792 (1)	831 (1)	856 (1)
ρ	D	P	·54	D	P	·56	..
$\overline{\Delta\nu}$	915 (1)	948 (0)	968 (2)	1028 (0)	1051 (1)	1070 (2)	1129 (6)
ρ	·80	D	·71	..	P	P	·53
$\overline{\Delta\nu}$	1167 (2)	1178 (2)	1217 (2)	1250 (4)	1318 (0)	1362 (6)	1386 (0)
ρ	D	D	·81	·82	D	·74	D
$\overline{\Delta\nu}$	1417 (0)	1441 (6)	1447 (0)	1710 (4 *b*)	2842 (8)	2930 (2)	2946 (2)
	D	·81	..	·61	·47	·57	·57

TABLE V.

Trans-*β*-*Decalol* (*Solid*).

No.	λ	$\bar{\nu}$	I	Assignment
1	4223·57	23670	0	$k \rightarrow$1035
2	4241·27	23571	0	$k \rightarrow$1134
3	4262·39	23455	1	k–1250
4	4279·66	23360	1	k–1345
5	4296·82	23266	1	k–1439 i–1250
6	4309·576	23198	0	k–1507
7	4570·67	21873	6	k–2832
8	4580·25	21827	(3)	k–2878
9	4588·41	21787	6	k–2918
10	4611·3	21680	0	i–2836
11	4629·1	21597	0	i–2919

$\overline{\Delta\nu}$ = 1035 (0), 1134 (0), 1250 (1), 1345 (1), 1439 (1), 1507 (0), 2834 (6), 2878 (3), 2918 (6)

TABLE VI.

Naphthalene.

No.	λ	$\bar{\nu}$	I	Assignment	No.	λ	$\bar{\nu}$	I	Assignment
1	5029·44	19877	(4)	*e*–3061	23	4394·88	22747	(1) *br*	*e*–191
2	4679·85	21362	(5)	*e*–1576	24	2322·59	43128	(4)	*k*–1577
3	4669·12	21411	(½)	*e*–1527 ?	25	4320·57	23139	(2)	*i*–1377
4	4658·89	21458	(2)	*k*–3247 } *i*–3058 }	26	4314·65	23170	(0)	*k*–1535
5	4654·71	21478	(4)	*e*–1460	27	4301·07	23244	(3)	*k*–1461
6	4650·96	21495	(2)	*e*–1443	28	4295·74	23272	(1)	*k*–1433
7	4644·49	21525	(0)	*e*–1413 ?	29	4289·03	23309	(0)	*k*–1396
8	4636·99	21560	(15)	*e*–1378	30	4285·54	23328	(15)	*k*–1377
9	4625·92	21611	(2)	*e*–1327 } *f*–1378 }	31	4276·5	23381	(0)	*k*–1324
10	4618·96	21644	(3)	*k*–3061	32	4263·12	23450	(2)	*k*–1255
11	4614·57	21680	(2)	*e*–1258	33	4260·21	23467	(1)	*k*–1238
12	4607·29	21699	(1)	*e*–1239	34	4255·0	23495	(0)	*k*–1210
13	4601·2	21735	(0)	*e*–1203	35	4243·09	23561	(2)	*k*–1144
14	4586·04	21799	(2)	*e*–1139	36	4221·66	23681	(4)	*k*–1024
15	4562·05	21914	(5)	*e*–1024	37	4208·39	23755	(1)	*k*–945
16	4544·23	22000	(2)	*e*–938	38	4177·24	23932	(1)	*k*–773
17	4509·75	22168	(1)	*e*–770	39	4174·71	23946	(5)	*k*–759
18	4507·59	22178	(6)	*e*–760	40	4169·42	23977	(½)	*k*–728
19	4500·09	22212	(1)	*e*–726	41	4165·33	24001	(½)	*i*–511
20	4457·57	22427	(6)	*e*–511	42	4138·96	24154	(½)	*p*–3244
21	4446·46	22484	(0)	*f*–511	43	4131·89	24195	(6)	*k*–510
22	4434·60	22542	(1)	*e*–396 } *m*–3050 }	44	4124·36	24239	(½)	*o*–3054
					45	4114·92	24305	(1)	*k*–400 } *p*–3050 }

$\overline{\Delta\nu}$	191 (1)	397 (1)	511 (6)	727 (1)	760 (6)	772 (1)
ρ	D	D	·65	D	·50	P
$\overline{\Delta\nu}$	941 (2)	1024 (5)	1142 (2)	1206 (0)	1239 (1)	1258 (2)
ρ	P	·55	·77	D	D	·77
$\overline{\Delta\nu}$	1326 (1)	1378 (15)	1406 ?	1438 (2)	1460 (4)	
ρ	P	·34	..	D	·64	
$\overline{\Delta\nu}$	1530 (0)	?1576 (5)	3058 (4)	3244 (2)		
ρ	D	·82	·55	D		

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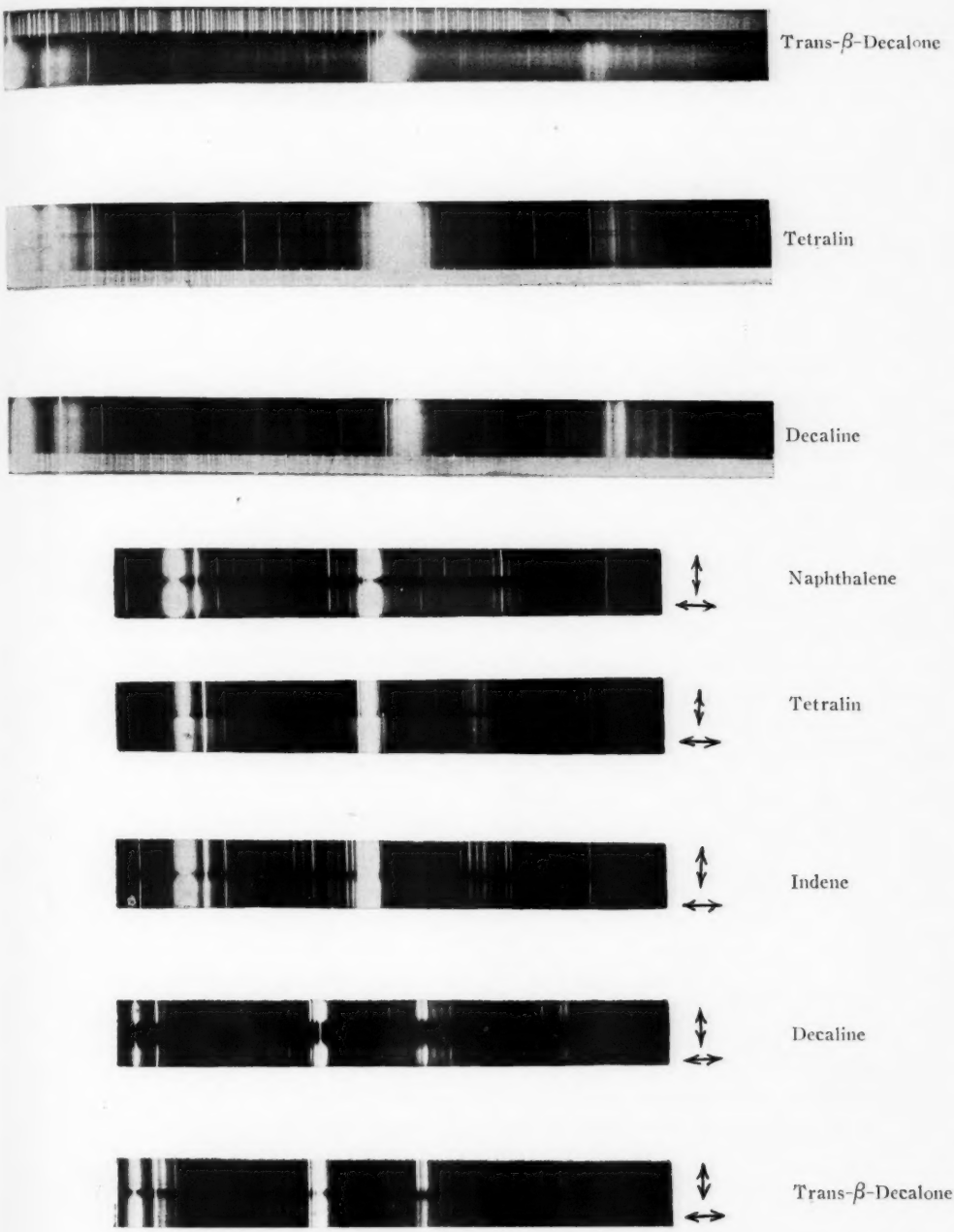

State of Polarisation.

UNIV. OF MICH.

THE NORMAL MODES AND FREQUENCIES OF THE SULPHUR MOLECULE.

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1. Normal Modes.

The model[1] assumed for sulphur molecule is that of a puckered octagon made up of two equal squares one turned through 45° with respect to the other. The planes of the two squares are parallel but not coincident. The atoms in the molecule occupy the corners of the puckered octagon. Let these atoms be denoted by the numbers 1, 2, 3, 4, 5, 6, 7, 8 as shown in Fig. 1. The valence bonds are along (15), (25), (26), (36), (37), (47), (48), (81). Let XYZ be three rectangular axes through the centre of gravity of the molecule. X-axis is parallel to (86), Y-axis is parallel to (75) and Z-axis is perpendicular to the planes of the two squares. Let $2a$ be the side of a square and $2c$ be the distance between the two squares. The co-ordinates of the atoms, when referred to the above set of axes can be given in terms of a and c.

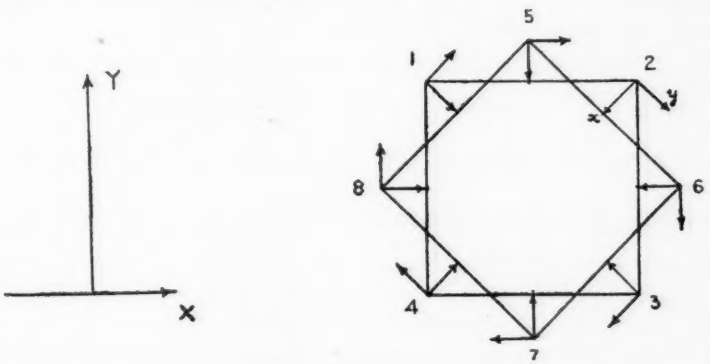

Fig. 1.

In determining the potential energy and the kinetic energy of the molecule in any mode of oscillation, it will however be found useful to express the

[1] Warren, B. E., and Burwell, J. T., *Jour. Chem. Phys.*, 1935, **3**, 6.

co-ordinates of any atom referred to its equilibrium position as the origin. Accordingly the 24 co-ordinates q are shown in Fig. 1. x_i, y_i, z_i are the co-ordinates of the ith atom with its equilibrium position as the origin. x_i points towards the centre of the square in which the ith atom is situated and z_i is measured perpendicular to the plane of the square and is taken positively on the side opposite to the centre of gravity of the molecule. We assume that the vibrations of the molecule are of small amplitude compared to the inter-atomic distances. Accordingly the kinetic and potential energies are of the form

$$2\,T = \Sigma\, m_i\, \dot{q}_i^2 \text{ and } 2\,V = \Sigma\, a_{ij}\, q_i\, q_j. \tag{1}$$

Expressions (1) can be simultaneously reduced to the form

$$2\,T = \Sigma\, \dot{Q}_k^2 \text{ and } 2\,V = \Sigma\, \lambda_k\, Q_k^2, \tag{2}$$

where Q's are linear combinations of the above q's. The former are called the normal co-ordinates and each Q corresponds to a normal mode. The λ's in the expression (2) are related to the normal frequencies ν_k by the equation

$$\lambda_k = 4\,\pi^2\,\nu_k^2. \tag{3}$$

If the coefficient λ of any normal co-ordinate Q is distinct from the other λ's the corresponding normal mode is non-degenerate. On the other hand, if two or more Q's have the same coefficient, the corresponding modes are degenerate and the degree of degeneracy is equal to the number of Q's which have the same coefficient λ.

Following Wigner[2] and Tisza,[3] Wilson[4] obtained the normal modes of vibrations of benzene by group theoretical methods. In the present paper we apply the same method to sulphur.

The symmetry operations of the model assumed for sulphur fall into seven classes. E_1 the identity ($h_1 = 1$), S^1 rotation reflection by $\pm \frac{\pi}{4}$ about the fourfold axis of rotation ($h_2 = 2$), C^2 rotation by $\pm \frac{\pi}{2}$ about the fourfold axis ($h_3 = 2$), S^3 rotation reflection by $\pm \frac{3\pi}{4}$ about the fourfold axis ($h_4 = 2$), C^4 rotation by π about the fourfold axis ($h_5 = 1$), σ_v reflection in a plane perpendicular to the planes of the squares and containing a diagonal of one of the squares ($h_6 = 4$), C_2 rotation by π about an axis through the centre of gravity of the molecule and passing through the middle points of two opposite valencies such as (15) and (37) ($h_7 = 4$).

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[2] *Göttinger Nachrichten*, 1930, 133.

[3] *Z. f. Phys.*, 1933, **82**, 48.

[4] *Phys. Rev.*, 1934, **45**, 706.

These operations form the group which may be given as a group of permutations on the 8 symbols 1, 2, 3, 4, 5, 6, 7, 8. The elements of this group are

E	
(15263748)	(14) (32) (75) (6) (8)
(18473625)	(24) (58) (76) (1) (3)
(1234) (5678)	(13) (65) (78) (2) (4)
(1432) (5876)	(27) (36) (18) (45)
(16453827)	(37) (28) (46 (15)
(17283546)	(38) (47) (25) (16)
(13) (24) (57) (68)	(26) (17) (35) (48)
(21) (34) (68) (7) (5)	

The above representation of the group is useful to obtain the normal co-ordinates but is not convenient for obtaining the conjugate classes of the group. By adopting the abstract form

$$P^8 = E, \quad Q^2 = E, \quad P\,Q = Q\,P^{-1}$$

the conjugate classes and the multiplication table of the conjugate classes may be written out. The character table given below is deduced therefrom by the usual methods.*

Character Table and Selection Rules.

	E	$2\,S^1$	$2\,C^2$	$2\,S^3$	C^4	$4\,\sigma_v$	$4\,C_2$	n_i	n_c'	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	1	2	2	P	*f*
A_2 ..	1	1	1	1	1	−1	−1	1	0	..	..
B_1 ..	1	−1	1	−1	1	1	−1	2	1	*f*	$M_\perp = 0$
B_2 ..	1	−1	1	−1	1	−1	1	1	1	*f*	*f*
E_1 ..	2	$\sqrt{2}$	0	$-\sqrt{2}$	−2	0	0	3	2	*f*	$M_z = 0$
E_2 ..	2	0	−2	0	2	0	0	3	3	D	*f*
E_3 ..	2	$-\sqrt{2}$	0	$\sqrt{2}$	−2	0	0	3	2	D	*f*
h_j ..	1	2	2	2	1	4	4				
χ_j' ..	24	0	0	0	0	2	0				
$h_j\,\chi_j'$ ..	24	0	0	0	0	8	0				
ψ_j' ..	18	0	−2	0	2	2	2				
$h_j\,\psi_j'$ ..	18	0	−4	0	2	8	8				

* This character table may also be obtained directly from the work of Tisza. In a preliminary communication to the *Physical Review*, the selection rules and the number of Raman lines to be expected for this molecule have been reported by one of us. (*Phys. Rev.*, 1938, 53, 1015.)

In the above table P stands for a polarized Raman line, D stands for a depolarized Raman line and f stands for a forbidden line. M denotes the electric moment. h_j is the number of the symmetry operations under the class j and χ_j' is the character of the operation under the class j in respect of the original set of co-ordinates. ψ_j' is the character obtained after allowing for pure rotation and translation. We have the following relationships :

$$\left.\begin{aligned}\chi_j' &= U_R\,(1 + 2\cos\phi_R)\\ \psi_j' &= (U_R - 2)\,(1 + 2\cos\phi_R)\end{aligned}\right\}$$ for operations R involving a pure rotation;

and $\chi_j' = \psi_j' = U_R\,(-1 + 2\cos\phi_R)$ for operations R involving rotation reflection.

U_R denotes the number of invariant atoms and ϕ_R is the angle of rotation for the operation R. The number of modes n_i under the representation i is obtained with the help of the relation

$$n_i = \frac{1}{N}\sum_j h_j\,\chi_j'\,\chi_j.$$

N is the order of the group and is 16 in this case. χ_j is the character of any operation under the class j in respect of the normal co-ordinates. The above relation includes pure rotations and translations. These may easily be excluded if we use alternatively

$$n_i' = \frac{1}{N}\sum_j h_j\,\psi_j'\,\chi_j.$$

It now follows from the table that the normal modes under the various representations are given by

$$2\,A_1 + A_2 + 2\,B_1 + B_2 + 3\,E_1 + 3\,E_2 + 3\,E_3.$$

The coefficient of each letter denotes the number of modes coming under that representation. If pure rotations and translations are eliminated, we get

$$2\,A_1 + B_1 + B_2 + 2\,E_1 + 3\,E_2 + 2\,E_3.$$

It therefore follows that if we use the normal co-ordinates, the determinant will split up into two linear factors (B_1, B_2) 5 quadratic factors of which two pairs are equal [A_1, E_1 (2), E_3 (2)] and 2 equal cubic factors [E_2 (2)]. The selection rules in respect of the modes coming under each representation are also given in the above table for both Raman and infra-red spectra. These are obtained from Tisza and Wigner. We may now see that the Raman spectrum of molecular sulphur should be expected to contain two strong and well polarized lines and five depolarized lines. None of these will be represented in the infra-red absorption. These conclusions are not affected by the type of forces that we may postulate later. It may be noted here that a complete lack of correlation between Raman and infra-red spectra usually

arises in the cases of molecules having a centre of inversion as one of the elements of symmetry. The case of sulphur comes apparently under this type although it does not possess a centre of inversion.

2. *Normal Co-ordinates.*

From the general theory of Wilson and Tisza, it is seen that every normal co-ordinate is associated with an irreducible representation of the group. The non-degenerate normal co-ordinates correspond to the irreducible representations of degree one (*i.e.*, the irreducible representations in which the identity element has character one) and they can be obtained immediately from the character table. We take the most general linear expression for Q in the 24 co-ordinates x_i, y_i, z_i and if R is an operation of the group, $RQ = \lambda Q$ where λ is the character corresponding to the operation R. These relations in general determine Q. For example, if

$$Q = \sum_{i=1}^{8} a_i x_i + \sum_{i=1}^{8} b_i y_i + \sum_{i=1}^{8} c_i z_i$$

is the normal co-ordinate corresponding to A_1, it follows that

$$a_1 = a_2 = a_3 = a_4, \quad a_5 = a_6 = a_7 = a_8$$

and similar expressions in b's and c's by C^2,

$$a_1 = a_5, \quad b_1 = b_5, \quad c_1 = c_5 \text{ by } C_2$$

and $a_1 = a_2, \quad b_1 = -b_2, \quad c_1 = c_2$ by σ_v.

Hence it follows that the most general linear expression which corresponds to A_1 is

$$Q = a_1 (x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8) + c_1 (z_1 + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 + z_8).$$

The normal co-ordinates Q_x, Q_y, Q_z, Q_{ω_x}, Q_{ω_y}, Q_{ω_z}, which correspond respectively to translations and rotations of the molecule as a whole can be obtained directly. For the determination of the normal co-ordinates of degeneracy r, we take r linear expressions $Q_1, Q_2, \cdots Q_r$ in the co-ordinates. If R is a group operation, we have

$$RQ_k = \lambda_{1k} Q_1 + \lambda_{2k} Q_2 + \cdots + \lambda_{rk} Q_r \; (k = 1, 2, \cdots r).$$

Using the fact that $\Sigma \lambda_{kk}$ is equal to the character of the group element R, we obtain certain relations which with the orthoganality relations between the coefficients of transformations (namely the sum of the product of coefficients of like terms in the expressions for two different normal co-ordinates is zero and the sum of the squares of the coefficients is unity for any normal co-ordinate) are in general sufficient to find a set of normal co-ordinates. For example, it follows from the character table that the normal

co-ordinates corresponding to E_2 will be of the form

$a_1 (x_1 + x_3 - x_2 - x_4) + a_2 (x_5 + x_7 - x_6 - x_8)$ + similar expressions in y's and z's.

Similarly those corresponding to E_1 and E_3 will be of the form

$a_1 (x_1 - x_3) + a_2 (x_2 - x_4) + a_3 (x_5 - x_7) + a_4 (x_6 - x_8)$ + similar expressions in y's and z's.

We find the degenerate Q's now by using the orthoganality relations. It may be noted that the set of 24 normal co-ordinates thus obtained is not unique but it is always possible to obtain at least one such set.

The following Q's wherever they belong to a linear factor of the secular equation are the normal co-ordinates. In other cases they are functions which must be combined with one or more others in order to obtain the normal co-ordinates. Q_3, Q_4 indicate the normal co-ordinates with frequencies ν_3 and ν_4, Q_1', Q_2' connected by a parenthesis indicate that two normal co-ordinates are obtained by forming two independent combinations of these with co-efficients which depend on the force constants. The corresponding frequencies ν_1 and ν_2 come under the class A_1. Wherever the Q's with dashes are connected by a parenthesis, similar combinations have to be formed in order to obtain the normal co-ordinates. Q_{5a}, Q_{5b} indicate two normal co-ordinates with the same frequency ν_5. Wherever Q's with suffixes a and b occur, a degeneracy is implied.

$$\left.\begin{aligned} Q_x &= (x_1 - x_3) - (x_2 - x_4) - \sqrt{2}\,(x_6 - x_8) + (y_1 - y_3) + \\ &\quad (y_2 - y_4) + \sqrt{2}\,(y_5 - y_7) \\ Q_y &= -(x_1 - x_3) - (x_2 - x_4) - \sqrt{2}\,(x_5 - x_7) + (y_1 - y_3) - \\ &\quad (y_2 - y_4) - \sqrt{2}\,(y_6 - y_8) \end{aligned}\right\} - E_1\ (2)$$

$$Q_z = z_1 + z_2 + z_3 + z_4 - z_5 - z_6 - z_7 - z_8 \quad \ldots\ldots \quad B_1$$

$$\left.\begin{aligned} Q_{\omega_x} &= c\,[x_1 - x_3) + (x_2 - x_4) - \sqrt{2}\,(x_5 - x_7) - (y_1 - y_3) + \\ &\quad (y_2 - y_4) - \sqrt{2}\,(y_6 - y_8] \\ &\quad + a\,[\sqrt{2}\,(z_1 - z_3) + \sqrt{2}\,(z_2 - z_4) - 2\,(z_5 - z_7)] \quad \ldots\ldots \\ Q_{\omega_y} &= c\,[(x_1 - x_3) - (x_2 - x_4) + \sqrt{2}\,(x_6 - x_8) + (y_1 - y_3) + \\ &\quad (y_2 - y_4) - \sqrt{2}\,(y_5 - y_7) + a\,[\sqrt{2}\,(z_1 - z_3) - \sqrt{2}\,(z_2 - z_4) \\ &\quad + 2\,(z_6 - z_8)] \quad \ldots\ldots \end{aligned}\right\} - E_3\ (2)$$

$$Q_{\omega_z} = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 \quad \ldots\ldots \quad A_2$$

$$\left.\begin{aligned} Q_1' &= x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8 \\ Q_2' &= z_1 + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 + z_8 \end{aligned}\right\} \ldots\ldots 2\,A_1$$

$$Q_3 = x_1 + x_2 + x_3 + x_4 - x_5 - x_6 - x_7 - x_8 \quad \ldots\ldots \quad B_1$$

$$Q_4 = y_1 + y_2 + y_3 + y_4 - y_5 - y_6 - y_7 - y_8 \quad \ldots\ldots \quad B_2$$

$$\left.\begin{aligned}
Q'_{5a} &= a\,[(x_1 - x_3) - (x_2 - x_4) - \sqrt{2}\,(x_6 - x_8) - (y_1 - y_3) - \\
&\qquad (y_2 - y_4) - \sqrt{2}\,(y_5 - y_7)] + c\,[-\sqrt{2}\,(z_1 - z_3) + \\
&\quad + \sqrt{2}\,(z_2 - z_4) + 2\,(z_6 - z_8)] \\
Q'_{6a} &= c\,[(x_1 - x_3) - (x_2 - x_4) - \sqrt{2}\,(x_6 - x_8) - (y_1 - y_3) - \\
&\qquad (y_2 - y_4) - \sqrt{2}\,(y_5 - y_7)] + a\,[\sqrt{2}\,(z_1 - z_3) - \\
&\qquad \sqrt{2}\,(z_2 - z_4) - 2\,(z_6 - z_8)] \\
Q'_{5b} &= a\,[(x_1 - x_3) + (x_2 - x_4) + \sqrt{2}\,(x_5 - x_7) + (y_1 - y_3) - \\
&\qquad (y_2 - y_4) - \sqrt{2}\,(y_6 - y_8)] + c\,[-\sqrt{2}\,(z_1 - z_3) - \\
&\qquad \sqrt{2}\,(z_2 - z_4) - 2\,(z_5 - z_7)] \\
Q'_{6b} &= c\,[(x_1 - x_3) + (x_2 - x_4) + \sqrt{2}\,(x_5 - x_7) + (y_1 - y_3) - \\
&\qquad (y_2 - y_4) - \sqrt{2}\,(y_6 - y_8)] + a\,[\sqrt{2}\,(z_1 - z_3) + \sqrt{2}\,(z_2 - z_4) \\
&\qquad + 2\,(z_5 - z_7)]
\end{aligned}\right\} -2\,E_1(2)$$

$$\left.\begin{aligned}
Q'_{7a} &= x_1 + x_3 - x_2 - x_4 + z_5 + z_7 - z_6 - z_8 \\
Q'_{8a} &= x_5 + x_7 - x_6 - x_8 - z_1 - z_3 + z_2 + z_4 \\
Q'_{9a} &= y_1 + y_3 - y_2 - y_4 + y_5 + y_7 + y_6 - y_8 \\
Q'_{7b} &= x_5 + x_7 - x_6 - x_8 + z_1 + z_3 - z_2 - z_4 \\
Q'_{8b} &= x_1 + x_3 - x_2 - x_4 - z_5 - z_7 + z_6 + z_8 \\
Q'_{9b} &= y_1 + y_3 - y_2 - y_4 - y_5 - y_7 + y_6 + y_8
\end{aligned}\right\} 3\,E_2\,(2)$$

$$\left.\begin{aligned}
Q'_{10a} &= (x_1 - x_3) - (x_2 - x_4) + \sqrt{2}\,(x_6 - x_8) - (y_1 - y_3) - \\
&\qquad (y_2 - y_4) + \sqrt{2}\,(y_5 - y_7) \\
Q'_{11a} &= a\,[(x_1 - x_3) - (x_2 - x_4) + \sqrt{2}\,(x_6 - x_8) + (y_1 - y_3) + \\
&\qquad (y_2 - y_4) - \sqrt{2}\,(y_5 - y_7)] + c\,[-\sqrt{2}\,(z_1 - z_3) + \\
&\qquad \sqrt{2}\,(z_2 - z_4) - 2\,(z_6 - z_8)] \\
Q'_{10b} &= (x_1 - x_3) + (x_2 - x_4) - \sqrt{2}\,(x_5 - x_7) + (y_1 - y_3) - \\
&\qquad (y_2 - y_4) + \sqrt{2}\,(y_6 - y_8) \\
Q'_{11b} &= a\,[(x_1 - x_3) + (x_2 - x_4) - \sqrt{2}\,(x_5 - x_7) - (y_1 - y_3) + \\
&\qquad (y_2 - y_4) - \sqrt{2}\,(y_6 - y_8)] + c\,[-\sqrt{2}\,(z_1 - z_3) - \\
&\qquad \sqrt{2}\,(z_2 - z_4) + 2\,(z_6 - z_8)]
\end{aligned}\right\} 2\,E_3\,(2)$$

Each of the above equations should be multiplied by the reciprocal of the sum of the squares of the coefficients of q's occurring in that equation.

3. *Modes of Oscillation.*

All the seventeen modes of oscillation are diagrammatically represented below. Those corresponding to pure rotations and translations may easily be identified.

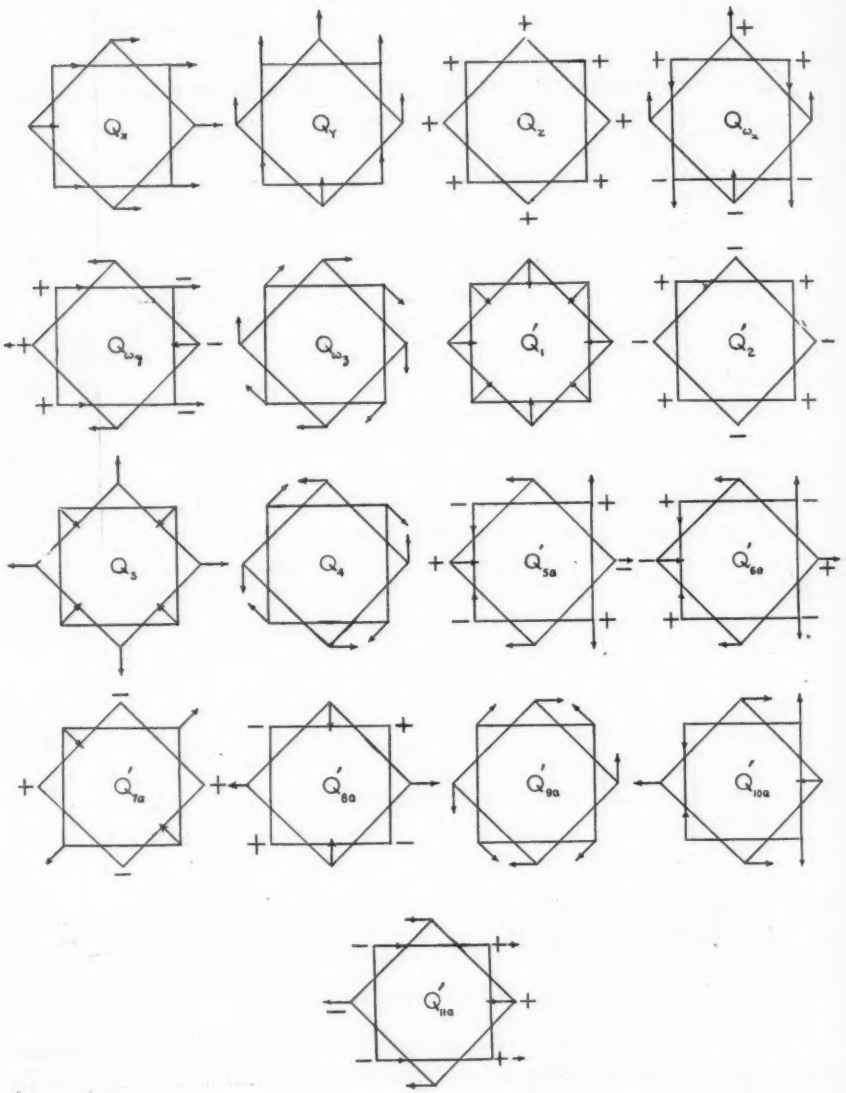
Q_0
Q_1
Q_2
Q_{ω_2}
Q_{ω_1}
Q_{ω_3}
Q'_1
Q'_2
Q_3
Q_4
Q'_{5a}
Q'_{6a}
Q'_{7a}
Q'_{8a}
Q'_{9a}
Q'_{10a}
Q'_{11a}

FIG. 2.

4. Potential Energy Function.

We will now form the potential energy function in terms of three types of forces, namely, the primary valence forces, the directed valence forces, and the repulsive forces between the distant atoms which are not directly bonded. K_1, K_2 and K_3 denote the respective force constants. The potential energy is the sum of three terms V_1, V_2 and V_3 given by

$$2V_1 = K_1[(\Delta R_{15})^2 + (\Delta R_{25})^2 + (\Delta R_{26})^2 + (\Delta R_{36})^2 + (\Delta R_{37})^2 + (\Delta R_{47})^2 + (\Delta R_{48})^2 + (\Delta R_{18})^2],$$

where ΔR_{ij} is the variation of the length of the valence bond connecting the ith and the jth atoms.

$$2V_2 = K_2[(\Delta\phi_1)^2 + (\Delta\phi_2)^2 + (\Delta\phi_3)^2 + (\Delta\phi_4)^2 + (\Delta\phi_5)^2 + (\Delta\phi_6)^2 + (\Delta\phi_7)^2 + (\Delta\phi_8)^2],$$

where $\Delta\phi_r$ is the variation of the angle between the two valence bonds at the rth atom.

$$2V_3 = K_3[(\Delta S_{12})^2 + (\Delta S_{23})^2 + (\Delta S_{34})^2 + (\Delta S_{41})^2 + (\Delta S_{56})^2 + (\Delta S_{67})^2 + (\Delta S_{78})^2 + (\Delta S_{85})^2],$$

where ΔS_{ij} is the variation of the distance of the ith and the jth atoms which are not directly bonded.

5. Calculation of the Frequencies.

The coefficient of any co-ordinate in the expressions for the Q's gives the component along that co-ordinate direction. These coefficients are proportional to the amplitudes of the motions of the atoms in the corresponding modes of vibration. We can therefore find the potential and kinetic energies of the molecule for any given mode and then obtain the frequencies, using Lagrange's equations of motion.

In the case of frequencies coming from a linear factor of the secular equation, the position of the atoms during an oscillation can be completely described by giving the value of one co-ordinate. For example,

$$Q_3 = x_1 + x_2 + x_3 + x_4 - x_5 - x_6 - x_7 - x_8$$

is the normal co-ordinates corresponding to B_1 and if in this mode of oscillation the amplitude of vibration is δ, each of the atoms 1, 2, 3, 4 undergoes a displacement δ towards the centre of the square (1234) and each of the atoms 5, 6, 7, 8 undergoes displacement δ away from the centre of the square (5678). The various lengths and angles in the displaced positions may easily

be evaluated and the variations written as

$$\Delta R_{15} = \Delta R_{25} = \Delta R_{36} = \Delta R_{37} = \Delta R_{47} = \Delta R_{48} = \Delta R_{18} = 0.$$

$$\Delta\phi_1 = \Delta\phi_2 = \Delta\phi_3 = \Delta\phi_4 = \frac{2\sqrt{2}\, a\delta}{R^2 \sin\phi}.$$

$$\Delta\phi_5 = \Delta\phi_6 = \Delta\phi_7 = \Delta\phi_8 = -\frac{2\sqrt{2}\, a\delta}{R^2 \sin\phi}.$$

ϕ is the angle between the two valence bonds at any atom in the equilibrium position.

$$\Delta S_{12} = \Delta S_{23} = \Delta S_{34} = \Delta S_{41} = -\sqrt{2}\,\delta$$
$$\Delta S_{56} = \Delta S_{67} = \Delta S_{78} = \Delta S_{85} = \sqrt{2}\,\delta.$$

Hence

$$2V_1 = 0, 2V_2 = \frac{64 a^2\delta^2}{R^4 \sin^2\phi} K_2, 2V_3 = 16 K_3 \delta^2$$

and the total potential energy is given by

$$2V = \frac{64 a^2\delta^2}{R^4 \sin^2\phi} K_2 + 16 K_3 \delta^2.$$

The kinetic energy is given by

$$2T = 8m\left(\frac{d\delta}{dt}\right)^2.$$

The equation of motion is

$$m \cdot \frac{d^2\delta}{dt^2} + \left(\frac{8 K_2 a^2}{R^4 \sin^2\phi} + 2 K_3\right)\delta = 0.$$

We now obtain λ_3 as

$$\lambda_3 = \frac{1}{m}\left(\frac{8 K_2 a^2}{R^4 \sin^2\phi} + 2 K_3\right).$$

ν_3 follows from the relation (3).

Similarly we find the other frequency relating to the second linear factor of the secular equation.

In the case of frequencies coming from quadratic or cubic factors of the secular equation, the treatment is slightly different. We have to take two different amplitudes corresponding to the two Q's giving the frequencies for the quadratic and similarly three for the cubic. We will work out the case of a quadratic factor (E_3) as an example. We have

$$Q'_{10} = (x_1 - x_3) - (x_2 - x_4) + \sqrt{2}(x_6 - x_8) - (y_1 - y_3) - (y_2 - y_4) + \\ + \sqrt{2}(y_5 - y_7)$$

$$Q'_{11a} = a\,[(x_1 - x_3) - (x_2 - x_4) + \sqrt{2}\,(x_6 - x_8) + (y_1 - y_3) + (y_2 - y_4) - \sqrt{2}\,(y_5 - y_7)]$$
$$+ c\,[-\sqrt{2}\,(z_1 - z_3) + \sqrt{2}\,(z_2 - z_4) - 2\,(z_6 - z_8)]$$

as the normal co-ordinates giving ν_{10} and ν_{11}. If the amplitude of vibration is δ in the first mode, all the atoms undergo a displacement equal to $\sqrt{2}\,\delta$ in the directions shown in the mode Q'_{10a}. If the amplitudes of vibration is β in the second mode, atom 1 moves through a distance $\sqrt{2}\ a\beta$ in the direction (12) and a distance $-\sqrt{2}\ c\beta$ in a direction perpendicular to the square (1234). The displacements in respect of the other atoms may be similarly obtained. The co-ordinates of the atoms in the displaced positions for the combined mode are given in the following table :

Atom	X co-ordinate	Y co-ordinate	Z co-ordinate
1	$-a + \sqrt{2}\,a\beta$	$a - \sqrt{2}\,\delta$	$c - \sqrt{2}\,c\beta$
5	$\sqrt{2}\,\delta - \sqrt{2}\,a\beta$	$\sqrt{2}\,a$	$-c$
2	$a + \sqrt{2}\,a\beta$	$a + \sqrt{2}\,\delta$	$c + \sqrt{2}\,c\beta$
6	$\sqrt{2}\,a - \sqrt{2}\,\delta - \sqrt{2}\,a\beta$	0	$-c + \sqrt{2}\,c\beta$
3	$a + \sqrt{2}\,a\beta$	$-a - \sqrt{2}\,\delta$	$c + \sqrt{2}\,c\beta$
7	$\sqrt{2}\,\delta - \sqrt{2}\,a\beta$	$-\sqrt{2}\,a$	$-c$
4	$-a + \sqrt{2}\,a\beta$	$-a + \sqrt{2}\,\delta$	$c - \sqrt{2}\,c\beta$
8	$-\sqrt{2}\,a - \sqrt{2}\,\delta - \sqrt{2}\,a\beta$	0	$-c - 2\,c\beta$

We evaluate the variations in lengths and angles as before and obtain

$$\Delta R_{15} = -\Delta R_{25} = -\Delta R_{37} = \Delta R_{47} = \frac{2a\delta - 2\sqrt{2}\ (a^2 + c^2)\,\beta}{R}$$

$$\Delta R_{26} = \Delta R_{36} = -\Delta R_{48} = -\Delta R_{18}$$
$$= \frac{2\,(\sqrt{2} - 2)\,\beta\,(a^2 + c^2) + 2\,(\sqrt{2} - 1)\,a\,\delta}{R}$$

$$\Delta\phi_5 = \Delta\phi_7 = 0$$

$$\Delta\phi_2 = \Delta\phi_3 = -\Delta\phi_1 = -\Delta\phi_4$$
$$= \frac{-2\sqrt{2}a\,\delta + (4 - 4\sqrt{2})\,(a^2 + c^2)\,\beta + \cos\phi\,[(4 - 2\sqrt{2})\,a\,\delta + (4 - 4\sqrt{2})\,(a^2 + c^2)\,\beta]}{R^2 \sin\phi}$$

$$\Delta\phi_6 = \Delta\phi_8 = \sqrt{2}\,\Delta\phi_1$$

$$\Delta S_{12} = \Delta S_{34} = 0\,;\ \Delta S_{23} = -\Delta S_{14} = 2\sqrt{2}\,\delta\,;\ \Delta S_{56} = \Delta S_{67} = -\Delta S_{78} = -\Delta S_{85} = 2\,\delta.$$

Hence the potential energy is

$$2\,V = \frac{4K_1}{R^2}\left[(16 - 8\sqrt{2})\,a^2\,\delta^2 + \beta^2\,(a^2 + c^2)^2\,(32 - 16\sqrt{2}) + a\,\delta\,\beta\,(a^2 + c^2)\,(32 - 32\sqrt{2})\right]$$
$$+ \frac{8\,K_2}{R^4 \sin^2\phi}\left[8(a + 2b\cos\phi)^2\,\delta^2 + 16\,p^2\,(1 - \cos\phi)^2\,\beta^2 + 16\sqrt{2}\,p\,(a + 2b\cos\phi)\,(1 - \cos\phi)\,\beta\,\delta\right]$$
$$+ 32\,K_3\,\delta^2,$$

where $p = (\sqrt{2} - 1)\,(a^2 + c^2)$.

The total kinetic energy is given by

$$2\,T = 16\,m\left[\left(\frac{d\delta}{dt}\right)^2 + (a^2 + c^2)\left(\frac{d\beta}{dt}\right)^2\right].$$

The corresponding determinant is easily obtained and is given in the next page. The two roots of this determinant give λ_{10} and λ_{11} from which we obtain ν_{10} and ν_{11}. Other frequencies are similarly calculated. The equations in respect of all the eleven modes of oscillation are listed below. k_1, k_2, k_3 used in these determinants are respectively identical with K_1, K_2, K_3 used in the rest of the paper.

λ_1 and λ_2 are the roots of

$$\begin{vmatrix} \frac{16b^2k_1}{R^2} + \frac{k_2}{\sin^2\phi}\left(\frac{2\sqrt{2}\,a}{R^2} - \frac{16a^2b}{R^4}\right)^2 + 2\,k_3 - m\,\lambda & \left|\begin{matrix} -\frac{16bck_1}{R^2} + \frac{16a^2ck_2}{R^4\sin^2\phi}\left(\frac{2\sqrt{2}a}{R^2} - \frac{16a^2b}{R^4}\right) \\ \frac{16c^2k_1}{R^2} + \frac{16^2a^4c^2k_2}{R^8\sin^2\phi} - m\lambda \end{matrix}\right| \\ \left|\begin{matrix} -\frac{16bck_1}{R^2} + \frac{16a^2ck_2}{R^4\sin^2\phi}\left(\frac{2\sqrt{2}a}{R^2} - \frac{16a^2b}{R^4}\right) \\ \frac{16c^2k_1}{R^2} + \frac{16^2a^4c^2k_2}{R^8\sin^2\phi} - m\lambda \end{matrix}\right| & \end{vmatrix} = 0$$

$$\lambda_3 = \frac{1}{m}\left(\frac{8k_2a^2}{R^4\sin^2\phi} + 2\,k_3\right)$$

$$\lambda_4 = \frac{4k_1\,a^2}{m\,R^2}$$

λ_5 and λ_6 are the roots of

$$\begin{vmatrix} [a^4(4-2\sqrt{2})+c^4(8+4\sqrt{2})+8a^2c^2]\frac{k_1}{R^2} & \frac{k_1ac}{R^2}[-2\sqrt{2}a^2-4(\sqrt{2}+1)c^2] \\ +\frac{2[2a^2-(1-\cos\phi)q]^2k_2}{R^4\sin^2\phi}+2a^2k_3-m\lambda(a^2+c^2) & +\frac{2k_2[2a^2-(1-\cos\phi)q][2ac+(1-\cos\phi)r]}{R^4\sin^2\phi}+2ack_3 \\ \hline \frac{k_1ac}{R^2}[-2\sqrt{2}a^2-4(\sqrt{2}+1)c^2] & \frac{2a^2c^2(2+\sqrt{2})k_1}{R^2}+\frac{2[2ac+(1-\cos\phi)r]^2k_2}{R^4\sin^2\phi} \\ +\frac{2k_2[2a^2-(1-\cos\phi)q][2ac+(1-\cos\phi)r]}{R^4\sin^2\phi}+2ack_3 & +2c^2k_3-m\lambda(a^2+c^2) \end{vmatrix} = 0$$

λ_7, λ_8 and λ_9 are the roots of

$$\begin{vmatrix} \frac{2a^2k_1}{R^2}+\frac{4(a\cos\phi+2b)^2k_2}{R^4\sin^2\phi}+2k_3-m\lambda & -\frac{2a(b+c)k_1}{R^2}+\frac{4(b+c)(1-\cos\phi)(a\cos\phi+2b)k_2}{R^4\sin^2\phi} & -\frac{2a(c-b)k_1}{R^2}+\frac{4(c-b)(1-\cos\phi)(a\cos\phi+2b)k_2}{R^4\sin^2\phi} \\ \hline -\frac{2a(b+c)k_1}{R^2}+\frac{4(b+c)(1-\cos\phi)(a\cos\phi+2b)k_2}{R^4\sin^2\phi} & \frac{4(b^2+c^2)k_1}{R^2}+\frac{8(1-\cos\phi)^2(b^2+c^2)k_2}{R^4\sin^2\phi}-m\lambda & O \\ \hline -\frac{2a(c-b)k_1}{R^2}+\frac{4(c-b)(1-\cos\phi)(a\cos\phi+2b)k_2}{R^4\sin^2\phi} & O & \frac{4(b^2+c^2)k_1}{R^2}+\frac{8(1-\cos\phi)^2(b^2+c^2)k_2}{R^4\sin^2\phi}-m\lambda \end{vmatrix} = 0$$

λ_{10} and λ_{11} are the roots of

$$\begin{vmatrix} \frac{(4-2\sqrt{2})a^2k_1}{R^2} + \frac{4(a+2b\cos\phi)^2k_2}{R^4\sin^2\phi} + 2k_3 - m\lambda & \frac{(4-4\sqrt{2})\,a\,(a^2+c^2)k_1}{R^2} + \frac{4\sqrt{2}\,p\,(a+2b\cos\phi)\,(1-\cos\phi)k_2}{R^4\sin^2\phi} \\ \frac{(4-4\sqrt{2})\,a\,(a^2+c^2)k_1}{R^2} + \frac{4\sqrt{2}\,p(a+2b\cos\phi)\,(1-\cos\phi)k_2}{R^4\sin^2\phi} & \frac{(8-4\sqrt{2})\,(a^2+c^2)^2k_1}{R^2} + \frac{8p^2\,(1-\cos\phi)^2k_2}{R^4\sin^2\phi} - m\lambda\,(a^2+c^2) \end{vmatrix} = 0$$

In the above equations

$$2b = (\sqrt{2}-1)a$$

$$p = (\sqrt{2}-1)\,(a^2+c^2)$$

$$-\cos\phi = \frac{2\,(\sqrt{2}-1)\,a^2 - 4\,c^2}{R^2}$$

$$q = (2+2\sqrt{2})\,c^2 + \sqrt{2}\,a^2$$

$$r = (2+\sqrt{2})\,ac$$

6. *Summary.*

The normal modes and frequencies of the sulphur molecule have been worked out on the assumption that the eight atoms in the molecule occupy the corners of a puckered octagon. There are eleven modes of which four are single and seven are doubly degenerate. Two of the former type and five of the latter type are Raman active. One is inactive in both Raman and infra-red spectra and the others are active only in infra-red absorption. The result obtained in respect of the Raman effect of sulphur are in agreement with the above conclusions.

Detailed expressions are derived for the normal frequencies by postulating three types of forces, namely, primary valence, directed valence and repulsive forces.

RAMAN SPECTRUM AND SPECIFIC HEAT OF SULPHUR.

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1. *Frequencies and Force Constants.*

The equations relating to all the eleven vibrational frequencies that are to be expected of the sulphur molecule when it is regarded as a puckered octagon have been given in a previous paper.* Only seven of these are active in Raman effect and three others are active in infra-red absorption. There is one frequency which is inactive in both Raman effect and infra-red absorption. None of the Raman frequencies are to be expected in the infra-red absorption and *vice versa*. Of the seven frequencies that are to be expected in Raman effect, two come under the total symmetric class (A_1) and should accordingly give rise to two strong and well polarised Raman lines. The Raman spectrum of sulphur[1] does exhibit two strong and well polarised lines at 470 and 216 and these may at once be identified with ν_1 and ν_2 in the notation of the paper already cited. We may now substitute these in the quadratic for λ_1 and λ_2 and obtain approximate values for K_1 and K_2 if we provisionally assume a zero value for K_3. If these are substituted in the expression for ν_7, a value which is in the neighbourhood of 243 is obtained for it. Thus, ν_1, ν_2 and ν_7 are respectively identified with 470, 216 and 243. Using these values, K_1, K_2 and K_3 may be obtained as $K_1 = 2 \cdot 309 \times 10^5$ dynes/cm.; $K_2 = 0 \cdot 903 \times 10^{-11}$ dynes cm./radian; $K_3 = 0 \cdot 0665 \times 10^5$ dynes/cm. K_1, K_2 and K_3 respectively represent the force constants in respect of the primary valence, directed valence and repulsive forces. This set of force constants is used to calculate all the frequencies. The values thus calculated are compared below in Table I with the observed values. Data in respect of infra-red absorption are taken from Barnes.[2] A better agreement may have been obtained by altering the constants slightly but the labour involved will be considerable and it is therefore not attempted.

The dimensions of the molecule are taken from the work of Warren and Burwell.

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* See preceding paper in this *Journal*.

[1] C. S. Venkateswaran, *Proc. Ind. Acad. Sci.*, (A), 1937, **4**, 345.

[2] *Phys. Rev.*, 1932, **39**, 562.

TABLE I. *Normal Frequencies of Sulphur.*

Class	Frequency calculated cm.$^{-1}$	Frequency observed cm.$^{-1}$	
		Infra-red	Raman
A_1	481	*f*	470 (P)
	197	*f*	216 (P)
B_1	255	267 (w)	*f*
B_2	557	*f*	*f*
E_1	481	465 (st)	*f*
	181	200 (st)	*f*
E_2	243	*f*	243
	456	*f*.	434 (D)
	122	*f*	152 (D)
E_3	542	*f*	114 (?)
	211	*f*	185

In the above Table *f* stands for forbidden, D for a depolarised and P for a well-polarised Raman line. The available polarisation data in respect of Raman lines are included. The intensities of infra-red absorption are indicated in brackets. It may be noted that only two well-polarised Raman lines are observed and of the other five, data available show that two are depolarised. These results are in perfect agreement with what may be expected of the proposed model. All the observed Raman frequencies except the one at 88 have been listed in the above table. Venkateswaran has given good reasons to show that this low frequency is characteristic of the lattice and hence need not be considered here. There is fair agreement between the calculated and observed frequencies in all cases except the one at 542. No line is reported in the neighbourhood of 542 but a weak line has been recorded by Venkateswaran at 114. It is possible that this line at 114 also belongs to the lattice and not to the molecule. In such a case another Raman line in the neighbourhood of 542 is to be expected. Of the various infra-red absorption maxima recorded by Barnes, the two strong ones at 465 and 200 are satisfactorily explained and these are to be regarded as fundamentals. Another weak absorption at 267 is also presumably a fundamental. Other absorption maxima have to be explained as combination tones or overtones.

The relatively small value of K_3 shows that the primary valence and the directed valence forces are the more important ones. This inference is in agreement with the observations of Badger.[3] The value of K_1 obtained in this molecule suggests that the adjacent sulphur atoms are bound to each other by single bonds. Utilising this value, we may calculate the S–S frequency with the help of the relation $\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$, where μ is the reduced mass. When expressed in wave-numbers, this comes out as 496 and compares well with 512 observed in disulphides containing this group.[4] If we take the force constant for S = S as twice the value of K_1, *i.e.*, $4 \cdot 618 \times 10^5$ dynes/cm., the corresponding frequency comes out as 702 and agrees well with the vibrational frequency 724 of sulphur vapour obtained from the band spectrum data.

2. Specific Heat of Sulphur.

The specific heat at any temperature consists of two parts arising respectively from the rotational and translational motions and the internal vibrations. Following the recent work of Lord, Ahlberg and Andrews,[5] we will assume that the former is represented by $2D\left(\frac{\theta}{T}\right)$, where D is the Debye function and θ is the mean effective characteristic temperature in respect of longitudinal and torsional elastic waves. The value of this is assumed to be 74·5 for sulphur and it corresponds to $\nu = 52$ cm.$^{-1}$. The exact relationship of θ to the observed Raman frequencies in the region of lattice oscillations is not discussed here. The eleven internal vibration frequencies are taken as 152 (2), 185 (2), 200 (2), 216 (1), 243 (2), 267 (1), 434 (2), 465 (2), 470 (1), 542 (2), 557 (1), and an Einstein function is associated with each one of them. The number in parenthesis represents the degree of degeneracy in each case. The sum of all the Einstein functions is the contribution of the latter type to the specific heat. The specific heat thus calculated is compared with the observed specific heat[6] at different temperatures in Table II.

Satisfactory and general agreement between the observed and calculated specific heats is noticed. At temperatures higher than 50° K the observed value is always somewhat larger than the calculated one. This may be due to the fact that the former refers to constant pressure whereas the calculations refer only to constant volume. The recent work of Sirkar and

[3] *Jour. Chem. Phys.*, 1935, **3**, 710.
[4] S. Venkateswaran, *Ind. Jour. Phys.*, 1931, **6**, 5.
[5] *Jour. Chem. Phys.*, 1937, **5**, 649.
[6] Values are taken from *I.C.T.*, **5** ; Nernst, *Ann. d. Phys.*, 1911, **36**, 395.

TABLE II. *Specific Heat of Sulphur.*

Temperature K	2D $\left(\frac{74\cdot5}{T}\right)$	Vibrational contribution	C_v Specific heat calc. (total)	C_p Observed
10	1·96	0	1·96	2·48
20	6·50	0·01	6·51	5·76
30	8·94	0·23	9·17	9·20
40	10·08	1·02	11·10	11·26
50	10·70	2·38	13·08	14·16
60	11·04	4·08	15·12	16·64
70	11·26	5·88	17·14	19·04
80	11·40	7·61	19·01	21·44
90	11·50	9·40	20·90	23·52
100	11·58	11·04	22·62	25·60
150	11·76	17·95	29·71	32·88
200	11·82	22·90	34·72	37·52
250	11·86	26·27	38·13	41·04
300	11·88	28·58	40·46	44·56

Gupta[7] may be referred to in this connection. Their calculations are however incomplete as they have not taken account of all the vibrational frequencies.

3. *Summary.*

Using the expressions derived by us in an earlier paper for the vibrational frequencies of the sulphur, the force constants K_1, K_2 and K_3 referring respectively to primary valence, directed valence and repulsive forces are evaluated. The values obtained are $K_1 = 2\cdot309 \times 10^5$ dynes/cm.; $K_2 = 0\cdot903 \times 10^{-11}$ dynes cm./radian and $K_3 = 0\cdot06665 \times 10^5$ dynes/cm. The frequencies calculated on the basis of these constants are compared with the observed Raman lines and infra-red absorption maxima and satisfactory agreement obtained.

The specific heat of sulphur is represented as the sum of a Debye function and a number of Einstein functions associated with the various normal frequencies. The calculated values compare favourably with the observed specific heats.

[7] *Ind. Journ. Phys.*, 1938, **12**, 145.

THE NORMAL FREQUENCIES OF PHOSPHORUS (P_4).

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Received August 1, 1938.

1. *Character Table.*

The structure assumed for the P_4 molecule is that of a regular tetrahedron, the atoms being situated at its corners. Evidence from various fields of investigation is strongly in favour of such a structure and hence other possibilities are not considered here. The model belongs to the tetrahedral point group T_d. The character table and the selection rules appropriate to this group are given below.

T_d Group.

T_d	E	$8C_3$	$3C_2$	6σ	$6S_4$	n_j	n'_j	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	1	P	f
A_2 ..	1	1	1	−1	−1	0	0	..	..
E ..	2	−1	2	0	0	1	1	D	f
F_1 ..	3	0	−1	−1	1	1	0	..	..
F_2 ..	3	0	−1	1	−1	2	1	D	active
h_j ..	1	8	3	6	6				
χ_j' ..	12	0	0	2	0				
$h_j \chi_j'$ ..	12	0	0	12	0				
ψ'_j ..	6	0	2	2	0				
$h_j \psi_j'$ ..	6	0	6	12	0				

The notation employed is the same as that already given in earlier papers by us in these *Proceedings*. It is seen from the table that we should expect three normal frequencies one of them being single, one doubly degenerate and one triply degenerate. All the three are active in Raman effect whereas only one is active in infra-red absorption. Of the three lines that are to be accordingly expected in Raman effect, the single frequency coming under the total symmetric class A_1 should be perfectly polarised and the remaining two

being degenerate should be completely depolarised. The experimental results[1] in respect of the Raman effect in phosphorus are in entire agreement with the above conclusions.

2. Normal Co-ordinates and Modes.

The principal axes, X, Y, Z, are shown in Fig. 1. They are obtained by joining the middle points of opposite sides of the tetrahedron and the positive directions are indicated by the letters X, Y, Z. The co-ordinates of each

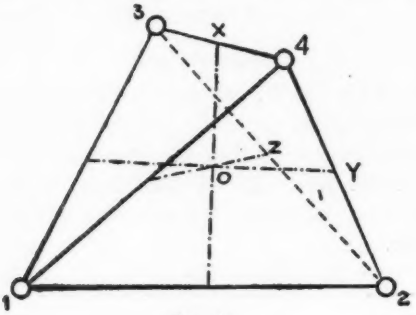

FIG. 1.

atom in any mode of oscillation are expressed with respect to a parallel co-ordinate system with the equilibrium position of the atom as the origin. The normal co-ordinates derived from the character table and the orthogonality relations are given below. The first six relate to pure translations and rotations.

$$\left.\begin{aligned} Q_x &= x_1 + x_2 + x_3 + x_4 \\ Q_y &= y_1 + y_2 + y_3 + y_4 \\ Q_z &= z_1 + z_2 + z_3 + z_4 \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad F_2\ (3)$$

$$\left.\begin{aligned} Q_{\omega x} &= y_1 - y_2 - y_3 + y_4 + z_1 - z_2 + z_3 - z_4 \\ Q_{\omega y} &= x_1 - x_2 - x_3 + x_4 + z_1 + z_2 - z_3 - z_4 \\ Q_{\omega z} &= x_1 - x_2 + x_3 - x_4 + y_1 + y_2 - y_3 - y_4 \end{aligned}\right\} \quad \ldots \quad \ldots \quad F_1\ (3)$$

$$Q_1 = x_1 + x_2 - x_3 - x_4 + y_1 - y_2 + y_3 - y_4 + z_1 - z_2 - z_3 + z_4 \qquad A_1$$

$$\left.\begin{aligned} Q_{2a} &= y_1 - y_2 + y_3 - y_4 - z_1 + z_2 + z_3 - z_4 \\ Q_{2b} &= 2x_1 + 2x_2 - 2x_3 - 2x_4 - y_1 + y_2 - y_3 + y_4 - z_1 + z_2 + z_3 - z_4 \end{aligned}\right\} E\ (2)$$

$$\left.\begin{aligned} Q_{3a} &= y_1 - y_2 - y_3 + y_4 + z_1 - z_2 + z_3 - z_4 \\ Q_{3b} &= x_1 - x_2 - x_3 + x_4 + z_1 + z_2 - z_3 - z_4 \\ Q_{3c} &= x_1 - x_2 + x_3 - x_4 + y_1 + y_2 - y_3 - y_4 \end{aligned}\right\} \quad \ldots \quad \ldots \quad F_2\ (3)$$

[1] S. Bhagavantam, *Ind. Jour. Phys.*, 1930, **5**, 35; C. S. Venkateswaran, *Proc. Ind. Acad. Sci.*, 1937, **4**, 345.

The modes of oscillation in respect of Q_1, Q_{2a} and Q_{3a} are shown diagrammatically in Fig. 2. In the case of Q_1, the actual displacements which each atom undergoes are shown. In the other two modes, the components

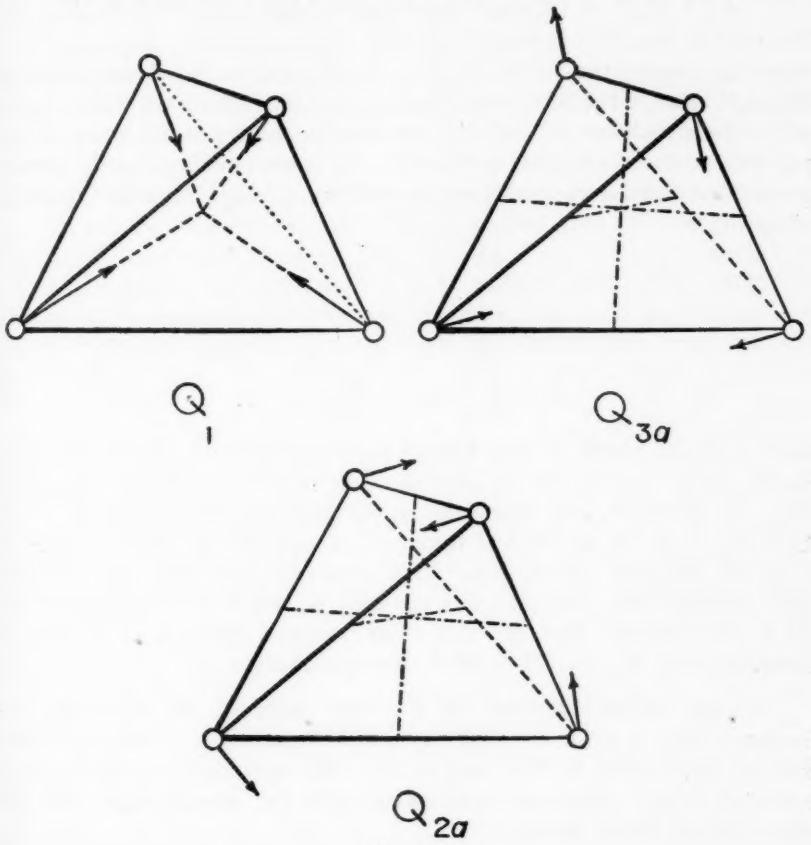

FIG. 2.

of the displacements of each atom along the three axes are shown separately. The representation follows closely the method adopted by Born[2] in connection with AB_4 molecules.

3. Potential Energy Function and Normal Frequencies.

The potential energy function chosen involves primary valence and directed valence forces and is given by:

[2] *Optik*, Julius Springer, 1933.

$$2V = K_1[(\Delta R_{12})^2 + (\Delta R_{13})^2 + (\Delta R_{14})^2 + (\Delta R_{23})^2 + (\Delta R_{24})^2 + (\Delta R_{34})^2] + K_2[(\Delta \phi_{213})^2 + (\Delta \phi_{214})^2 + (\Delta \phi_{314})^2 + (\Delta \phi_{123})^2 + (\Delta \phi_{124})^2 + (\Delta \phi_{324})^2 + (\Delta \phi_{132})^2 + (\Delta \phi_{134})^2 + (\Delta \phi_{234})^2 + (\Delta \phi_{142})^2 + (\Delta \phi_{143})^2 + (\Delta \phi_{243})^2].$$

where R_{ij} denotes the distance between the ith and the jth atoms and ϕ_{ijk} is the angle between the two valence bonds ij and jk. In all the three normal modes the variations ΔR and $\Delta\phi$ are then calculated in the usual manner and the potential energies evaluated. The corresponding kinetic energies are written down and the following relations obtained from the equations of motion

$$\lambda_1 = \frac{4K_1}{m}$$

$$\lambda_2 = \frac{1}{m}\left[K_1 + \frac{6K_2}{R^2}\right]$$

$$\lambda_3 = \frac{1}{m}\left[2K_1 + \frac{8K_2}{R^2}\right] \quad .. \quad .. \quad .. \quad (1)$$

where R is the length of each valence bond and m is the mass of the phosphorus atom. ν_1, ν_2 and ν_3 corresponding respectively to the representations A_1, E and F_2 may now easily be obtained from the relation $\lambda = 4\pi\nu^2$. Assuming ν_1 and ν_3 as 606 and 468 cm.$^{-1}$ respectively, we obtain ν_2 directly from the relations (1) as 344. This compares well with the observed value, namely 363. We may also evaluate K_1 and K_2 if we assign a value for R. We assume[3] that $R = 2{\cdot}21 \times 10^{-8}$ cm. and obtain $K_1 = 1{\cdot}68 \times 10^5$ dynes/cm. and $K_2 = 0{\cdot}396 \times 10^{-11}$ dynes cm./radian.

We can utilise the value of K_1 thus obtained for calculating the frequency that is to be expected of a P ≡ P molecule. Taking the force constant appropriate to this case as $3K_1$, the oscillation frequency may be evaluated as 742. This may be compared with the experimental value 779 obtained from band spectra.

4. *Specific Heat of Phosphorus.*

The specific heat of phosphorus is calculated at 9° C. by assigning 12 calories on account of the Debye functions and evaluating the three Einstein functions corresponding to the observed normal frequencies 606, 468, 363. The result obtained is 19·8 calories whereas the experimental value available[4]

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[3] Maxwell, Hendricks and Mosley, *Jour. Chem. Phys.*, 1935, **3**, 699.

[4] The value is taken from *Landolt Bornstein Tabellen* and is due to Ewald.

for yellow phosphorus at 9° C. is 22·0 calories. Experimental data in respect of the specific heat of phosphorus at different temperatures is not available.

5. *Summary.*

Assuming a potential energy function based on primary valence and directed valence forces, expressions are obtained by group theoretical methods for the normal frequencies of the tetrahedral molecule P_4. The numerical values of the observed frequencies are in agreement with the theoretical expressions and yield $K_1 = 1{\cdot}68 \times 10^5$ dynes/cm. and $K_2 = 0{\cdot}396 \times 10^{-11}$ dynes cm./radian for the primary valence and directed valence force constants respectively. On the assumption that this value of K_1 refers to a single bond, the oscillation frequency that is to be expected of P ≡ P molecule is calculated as 742 and compared with the value 779 obtained from band spectra. The calculated specific heat at 9° C. is 19·8 calories which is in good agreement with the experimental value, namely 22·0 calories.

DIFFRACTION OF LIGHT BY ULTRASONIC WAVES.

By K. Nagabhushana Rao.

Received July 21, 1938.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction.*

A theory of the diffraction of light by high-frequency sound waves was developed by Sir C. V. Raman and Mr. N. S. Nagendra Nath jointly, and later also by the latter independently, and was published in a series of papers in these *Proceedings*. (These will be referred to below for brevity as R.-N. I, II, III, IV, V and N. I). In a paper published in the *Physica*, July 1937 (referred to below as V. C.), Van Cittert has treated the case of normal incidence; starting from the usual expression for a pencil of light and considering the light fluctuations at successive points in the medium and thus also the diffraction effects, he obtains a system of differential equations, and solves them in a series of Bessel-functions of which the first term agrees with the simplified theory contained in R.-N. I. In the present paper it will be shown that the results of the more general theory of Raman and Nath (R.-N. IV and N. I) for the case of normal incidence are completely identical with those of Van Cittert. The latter's method is then extended to the case of oblique incidence and the results thus obtained are proved to be also in agreement with those of Raman and Nath for this case contained in their papers (R.-N. V and N. I). The solution is developed *in extenso*, as a series of Bessel-functions. The method of parts as developed in Mr. Nagendra Nath's recent paper for two systems of sound-waves is extended, and the resulting generalised difference-differential equation solved.

Notation.

μ_0' = Refractive index of the medium in the undisturbed state.

μ = Maximum variation of the refractive index from μ_0'.

λ = Wave-length of incident light.

λ^* = Wave-length of sound wave.

ν^* = Frequency of the sound wave.

$$n = \mu\,(y, t) = \mu_0' - \mu \sin 2\pi \left(\nu^* t - \frac{y}{\lambda^*}\right)$$

= refractive index of the medium.

2. *Normal and Oblique Incidence.*

Considering the case of normal incidence, the results of R.-N. IV, and those of V. C. are proved to be the same as follows :—

(*a*) The restrictions under which the results are valid.

(*b*) The angles of inclination of the various orders of spectra to a fixed line.

(*c*) The expressions for the intensities, must be the same in both the theories.

The incident light will be diffracted at angles given by $\sin\theta = \pm\frac{n\lambda}{\lambda^*}$ for the nth order (R.-N. IV), where θ is the angle with the x axis. Van-Cittert's theory also gives the same expression ($\sin i_n = \frac{n\lambda}{\lambda^*}$ where i_n is the angle of the nth order with the axis of x).

The difference-differential equation as in V. C. is :

$$\frac{dS_p}{d\xi} = -\frac{i\,(\mu_p - \mu_0)}{\nu_0}\,S_p + \tfrac{1}{2}\{S_{p-1} - S_{p+1}\}, \qquad (1)$$

where $\mu_p = \frac{2\pi\mu_0'}{\lambda}\cos r_p$, $\nu_p = \frac{2\pi\mu}{\lambda}\cos r_p$, and $\xi = \frac{2\pi\mu x}{\lambda}$.

$$-\left(\frac{\mu_p - \mu_0}{\nu_0}\right) = \frac{\mu_0'}{\mu}(1 - \cos r_p), \text{ and from the relation } \sin r_p = \frac{p\,\lambda}{n\lambda^*},$$

$$= \tfrac{1}{2}\,p^2 \cdot \frac{\lambda^2\mu_0'}{\mu n^2\lambda^{*2}} = \tfrac{1}{2}\,p^2 \cdot \frac{\lambda^2}{\mu\mu_0'\lambda^{*2}}$$

(neglecting powers of μ higher than the first)

$$= \tfrac{1}{2}\,p^2\beta \text{ where } \beta = \frac{\lambda}{\mu\mu_0'\lambda^{*2}}.$$

$\therefore$ The equation takes the form

$$\frac{dS_p}{d\xi} = -\frac{ip^2\beta}{2}\,S_p + \tfrac{1}{2}\{S_{p-1} - S_{p+1}\}. \qquad (2)$$

The solution of this equation is given as below (V. C.)

$$\left.\begin{aligned} S_0 &= J_0 - 2i\beta J_3 + 2\beta^2 J_4 + \cdots \\ S_1 &= J_1 + i\beta J_2 - \beta^2 J_3 + \cdots \\ S_2 &= J_2 + 5i\beta J_3 - 21\beta^2 J_4 + \cdots \\ S_3 &= J_3 + 14i\beta J_4 + \cdots \end{aligned}\right\} \text{where } J_n = J_n\left(\frac{2\pi\mu x}{\lambda}\right) \qquad (2a)$$

Expressing these in powers of ξ, we have

$$\left.\begin{aligned} S_0 &= 1 - \frac{\xi^2}{4} - \frac{i\beta\xi^3}{24} + \frac{\xi^4}{64}\left(1 + \frac{\beta^2}{3}\right) - \cdots \\ S_1 &= \frac{\xi}{2}\left\{1 + \frac{i\beta\xi}{4} - \left(1 + \frac{\beta^2}{3}\right)\frac{\xi^2}{8} + \cdots\right\} \\ S_2 &= \frac{\xi^2}{8}\left\{1 + \frac{5i\beta\xi}{6} - \tfrac{1}{4}\left(\frac{7\beta^2}{4} + \tfrac{1}{3}\right)\xi^2 + \cdots\right\} \\ S_3 &= \frac{\xi^3}{48}\left\{1 + \frac{7i\beta\xi}{4} + \cdots\right\} \end{aligned}\right\} \quad (2b)$$

Intensity $= |S_p|^2$ for the pth order.

R.-N. IV and N. I.

$$\left.\begin{aligned} \psi_0 &= 1 - \frac{\xi^2}{4} - \frac{i\rho\xi^3}{24} + \frac{1}{64}\left(1 + \frac{\rho^2}{3}\right)\xi^4 + \cdots \\ \psi_1 &= \frac{\xi}{2}\left\{1 + \frac{i\rho}{4}\xi - \frac{1}{24}(\rho^2 + 3)\xi^2 - \frac{i\rho}{192}(\rho^2 + 10)\xi^3 + \cdots\right\} \\ \psi_2 &= \frac{\xi^2}{8}\left\{1 + \frac{5i\rho}{6}\xi - \frac{1}{4}\left(\frac{7}{4}\rho^2 + \frac{1}{3}\right)\xi^2 + \cdots\right\} \\ \psi_3 &= \frac{\xi^3}{48}\left\{1 + \frac{7i\rho}{4}\xi + \cdots\right\} \end{aligned}\right\} \quad (2c)$$

Intensity of the pth order $= |\psi_p|^2$.

$\rho = \dfrac{\lambda^2}{\mu\mu_0'\lambda^{*2}} = \beta$ and ξ signifies the same in both. Hence the expressions for the intensities are the same. The difference-differential equation is the same in both the cases.

$$i.e., \quad |\psi_p|^2 = |S_p|^2. \quad (3)$$

μ is small and of the order of 10^{-5}. β must be less than 1.

$$\beta = \frac{\lambda^2}{\mu\mu_0'\lambda^{*2}} = 0\,(10^{-1}) < 1. \quad \therefore \ \rho < 1.$$

$$\left\{\begin{aligned} \lambda &= 0\,(10^{-5}) \\ \lambda^* &= 0\,(10^{-2}) \\ \mu &= 0\,(10^{-5}) \\ \mu_0' &= 0\,(1). \end{aligned}\right.$$

Thus ρ also satisfies the condition.

$\therefore$ The results for the case of normal incidence from the general theory (R.-N. IV and N. I) and of V. C. are thus the same.

For the case of oblique incidence, we first have the same equation (1).

$$\frac{dS_p}{d\xi} = -\frac{i\,(\mu_p - \mu_0)}{\nu_0} S_p + \tfrac{1}{2}\{S_{p-1} - S_{p+1}\}. \quad (3a)$$

The angles of emergence for the various orders are given by

$$\sin r_{p+1} - \sin r_p = \pm \frac{\lambda}{n\lambda^*}. \qquad \text{(V.C.)}$$

$$\sin r_p - \sin r_{p-1} = \frac{\lambda}{n\lambda^*}$$

$$\sin r_{p-1} - \sin r_{p-2} = \frac{\lambda}{n\lambda^*}$$

$$\sin r_1 - \sin r_0 = \frac{\lambda}{n\lambda^*}$$

$$\therefore \sin r_p - \sin r_0 = p \cdot \frac{\lambda}{n\lambda^*}.$$

Let the angle of incidence be ϕ ($i_0 = \phi$). We have the relation $\frac{\sin i_p}{\sin r_p} = n$ (refractive index of the medium).

$$\therefore \sin i_p = \sin\phi + p\frac{\lambda}{\lambda^*}. \qquad (3b)$$

This equation is the same as in R.-N. II (oblique incidence).

$$-\left(\frac{\mu_p - \mu_0}{\nu_0}\right) = \frac{\mu_0'}{\mu}\left\{\frac{\cos r_0 - \cos r_p}{\cos r_0}\right\}$$

$$\cos r_0 = \sqrt{1 - \frac{\sin^2\phi}{n^2}} = 1 \text{ (neglecting powers of } \phi \text{ higher than the first).}$$

$$\cos r_p = \sqrt{1 - \left(\frac{\sin\phi}{n} + p\frac{\lambda}{n\lambda^*}\right)^2}$$

$$= 1 - \frac{1}{2}\left\{\frac{p^2\lambda^2}{n^2\lambda^{*2}} + 2p\frac{\sin\phi\lambda}{n^2\lambda^*}\right\} \text{ (neglecting higher terms).}$$

$$\therefore -\left(\frac{\mu_p - \mu_0}{\nu_0}\right) = \frac{\mu_0'}{2\mu}\left\{p^2\frac{\lambda^2}{n^2\lambda^{*2}} + 2p\frac{\lambda\sin\phi}{n^2\lambda^*}\right\}$$

$$= \tfrac{1}{2}\left\{p^2\frac{\lambda^2}{\mu\mu_0'\lambda^{*2}} + 2p\frac{\lambda\sin\phi}{\mu\mu_0'\lambda^*}\right\}$$

Setting $\beta = \frac{\lambda^2}{\mu\mu_0'\lambda^{*2}}$ and $a = \frac{2\lambda\sin\phi}{\mu\mu_0'\lambda^*} = a\beta$ the equation becomes

$$2\frac{dS_p}{d\xi} = i\beta(p^2 + ap) + (S_{p-1} - S_{p+1}). \qquad (4)$$

[In deriving these equations, powers of ϕ higher than the first have been neglected : μ^2 is neglected. ϕ in this paper corresponds to $\pi + \phi$ in R.-N. V and N. I]. It can be easily seen that the diffraction pattern is asymmetric (R.-N. V).

3. The Difference-Differential Equation.

$$2\frac{dS_p}{d\xi} = C_p S_p + \{S_{p-1} - S_{p+1}\}, \tag{5}$$

where $C_p = i\beta\,((p^2 + \alpha p)$.

Substituting $S_p = J_p + \sum_1^\infty a_{p,n+p}\, J_{n+p}$ in equation (5), we get the following recurrence relations.

$$a_{0,1} = 0$$

$$a_{0,2} = 0$$

$$a_{0,n+1} - a_{0,n-1} = -\{a_{1,n} - a_{-1,n}\}.$$

$$a_{p,p+1} - a_{p-1,p} = C_p$$

$$a_{p,n+p+1} - a_{p-1,p+n} + a_{p+1,p+n} - a_{p,p+n-1} = C_p\, a_{p,p+n}$$

$$\therefore\ a_{p-1,n+p} - a_{p-2,p+n-1} + a_{p,p+n-1} - a_{p-1,p+n-2} = C_{p-1}\, a_{p-1,p+n-1}$$

. . . . . .

$$a_{1,n+2} - a_{0,n+1} + a_{2,n+1} - a_{1,n} = C_1\, a_{1,n+1}$$

On adding, we have

$$\boxed{a_{p,p+n+1} = a_{0,n+1} - a_{p+1,p+n} + a_{1,n} + \sum_1^p C_p\, a_{p,p+n}} \tag{6}$$

which can also be written as

$$\boxed{a_{p,p+n+1} = a_{0,n-1} = a_{p+1,p+n} + a_{-1,n} + \sum_1^p C_p\, a_{p,p+n}.} \tag{6a}$$

$$a_{p,p+1} - a_{p-1,p} = C_p$$

$$\therefore\quad \boxed{a_{p,p+1} = \sum_1^p C_p.} \tag{7}$$

$$a_{p,p+2} = \sum_1^p C_p\, a_{p,p+1}$$

$$= \sum_1^p C_p\,(C_1 + C_2 + \cdots + C_p) = \tfrac{1}{2} \sum_{r=1}^{p} \sum_{s=1}^{p} C_r\, C_s.$$

$$= \tfrac{1}{2}\left\{\left(\sum_1^p C_r\right)^2 + \sum_1^p C_r^2\right\}.$$

$$\boxed{a_{p,\,p+2} = \tfrac{1}{2}\left\{\left(\sum_1^p C_r\right)^2 + \sum_1^p C_r^2\right\}} \qquad (7a)$$

$$a_{p,\,p+3} = a_{0,\,3} - \left\{C_2 + C_3 + \cdots + C_{p+1}\right\} + \sum_1^p C_p\, a_{p,\,p+2}.$$

$$a_{p,\,p+3} = -\left\{C_{-1} + \sum_1^{p+1} C_r\right\} + \sum_1^p C_r C_s C_t \rightarrow \text{(all like terms being counted once only)} \qquad (7b)$$

$$C_p = i\beta\,(p^2 + \alpha p).$$

$$\left.\begin{aligned}
a_{p,\,p+1} &= i\beta\left\{\frac{p\,(p+1)\,(2p+1)}{6} + \alpha\cdot\frac{p\,(p+1)}{2}\right\}\\
a_{p,\,p+2} &= -\frac{\beta^2}{2}\left\{\frac{p\,(p+1)\,(2p+1)\,(10p^3+33p^2+23p-6)}{180}\right.\\
&\qquad\left. + \frac{\alpha}{3}p^2\,(p+1)^2\,(p+2) + \frac{\alpha^2}{12}\,p\,(p+1)\,(p+2)\,(3p+1).\right\}\\
a_{p,\,p+3} &= -i\beta\left\{\frac{(p+1)\,(p+2)\,(2p+3)}{6} + 1 + \frac{\alpha}{2}p\,(p+3)\right\} + \sum_1^p C_p\, a_{p,\,p+2}
\end{aligned}\right\}$$

Expressions for the amplitudes $S_0, S_1, \cdots$ are as below :

$$\begin{aligned}
S_0 = {} & J_0 - 2i\beta J_3 + 2\beta^2\,(1+\alpha^2)\,J_4 + 2i\beta\,\{5 + \beta^2\,(1+3\alpha^2)\}\,J_5\\
& - 2\beta^2\,\{(27 + 9\alpha^2) + \beta^2\,(1 + 6\alpha^2 + \alpha^4)\}\,J_6\\
& - 2i\beta\,\{18 + \beta^2\,(113 + 119\,\alpha^2) + \beta^4\,(1 + 10\alpha^2 + 5\alpha^4)\}\,J_7\\
& + 2\beta^2\,\{(246 + 22\alpha^2) + \beta^2\,(459 + 922\alpha^2 + 55\alpha^4) + \beta^4\,(1 + 15\alpha^2\\
& + 15\alpha^4 + \alpha^6)\,J_8 + \cdots
\end{aligned}$$

$$\begin{aligned}
S_1 = {} & J_1 + i\beta\,(1+\alpha)\,J_2 - \beta^2\,(1+\alpha)^2\,J_3 - i\beta\,\{(6 + 2\alpha) + \beta^2\,(1+\alpha)^3\}J\\
& + \beta^2\,\{(28 + 30\alpha + 10\alpha^2) + \beta^2\,(1+\alpha)^4\}\,J_5 + i\beta\,\{(25 + 3\alpha)\\
& + \beta^2\,(114 + 196\alpha + 122\alpha^2 + 24\alpha^3) + \beta^4\,(1+\alpha)^5\}\,J_6\\
& - \beta^2\,\{(273 + 190\alpha + 31\alpha^2) + \beta^2\,(460 + 1044\alpha + 928\alpha^2 + 364\alpha^3\\
& + 56\alpha^4) + \beta^4\,(1+\alpha)^6\}\,J_7 + \cdots
\end{aligned}$$

$$\begin{aligned}
S_2 = {} & J_2 + i\beta\,(5 + 3\alpha)\,J_3 - \beta^2\,(21 + 24\alpha + 7\alpha^2)\,J_4 - i\beta\,\{(15 + 5\alpha)\\
& + \beta^2\,(85 + 141\alpha + 79\alpha^2 + 15\alpha^3)\}\,J_5\\
& + \beta^2\,\{(214 + 176\alpha + 38\alpha^2) + \beta^2\,(341 + 738\alpha + 604\alpha^2 + 222\alpha^3\\
& + 31\alpha^4)\}\,J_6 + i\beta\,\{(39 + 16\alpha) + \beta^2\,(2291 + 2849\alpha + 1205\alpha^2\\
& + 175\alpha^3) + \beta^4(1364 + 3634\alpha + 3892\alpha^2 + 2096\alpha^3 + 568\alpha^4 +\\
& 62\alpha^5)\}\,J_7 + \cdots
\end{aligned}$$

$$S_3 = J_3 + i\beta\,(14 + 6\alpha)\,J_4 - \beta^2\,(147 + 120\alpha + 25\alpha^2)\,J_5 - i\beta\,\{(31 + 9\alpha) + \beta^2\,(1408 + 1662\alpha + 664\alpha^2 + 90\alpha^3)\}\,J_6 + \beta^2\,\{(973 + 618\alpha + 132\alpha^2) + \beta^2\,(13013 + 19910\alpha + 11566\alpha^2 + 3024\alpha^3 + 270\alpha^4)\}\,J_7 + \cdots$$

$$S_4 = J_4 + i\beta\,(30 + 10\alpha)\,J_5 - \beta^2\,(627 + 400\alpha + 65\alpha^2)\,J_6 - i\beta\,\{(56 + 14\alpha) + \beta^2\,(11440 + 10570\alpha + 3304\alpha^2 + 350\alpha^3)\}\,J_7 + \beta^2\,\{(3872 + 2114\alpha + 329\alpha^2) + \beta^2\,(653653 + 771990\alpha + 344570\alpha^2 + 68880\alpha^3 + 3770\alpha^4)\}\,J_8 + \cdots$$

$$S_5 = J_5 + i\beta\,(55 + 15\alpha)\,J_6 - \beta^2\,(2002 + 1050\alpha + 140\alpha^2)\,J_7 - i\beta\,\{(92 + 20\alpha) + \beta^2\,(61490 + 36830\alpha + 12054\alpha^2 + 1050\alpha^3)\}\,J_8 + \cdots$$

$$S_6 = J_6 + i\beta\,(91 + 21\alpha)\,J_7 - \beta^2\,(5378 + 2402\alpha + 266\alpha^2)\,J_8 - i\beta\,\{(141 + 21\alpha) + \beta^2\,(255098 + 155570\alpha + 36042\alpha^2 + 2646\alpha^3)\}J_9 + \cdots$$

$$S_7 = J_7 + i\beta\,\{(140 + 28\alpha)\}\,J_8 - \beta^2\,(12138 + 4704\alpha + 462\alpha^2)\,J_9 + \cdots$$

. . . . . .

$$S_p = J_p + i\beta\left\{\frac{p\,(p+1)\,(2p+1)}{6} + \frac{\alpha}{2}\,p\,(p+1)\right\}J_{p+1} - \frac{\beta^2}{2}\left\{\frac{p\,(p+1)\,(2p+1)\,(10p^3 + 33p^2 + 23p - 6)}{180} + \frac{\alpha}{3}\,p^2\,(p+1)^2\,(p+2) + \frac{\alpha^2}{4}\,p\,(p+1)\,(p+2)\,(3p+1)\right\}J_{p+2} + \cdots + a_{p,\,p+n}\,J_{p+n} + \cdots$$

where $J_n = J_n\left(\frac{2\pi\mu x}{\lambda}\right)$.

4. Systems of Parallel Sound Waves.

Let us consider the case of three systems of sound waves with different frequencies, amplitudes and wave-lengths. The refractive index of the medium is given by $\mu\,(y,\,t) = \mu_0 + \sum_{r=1}^{3} \mu_r \sin 2\pi\left(\nu_r^{*}\,t - \frac{y}{\lambda_r^{*}}\right)$. It can easily be proved that combinational orders are present and that they occur at angles given by $\left(\sin\theta = r\,\frac{\lambda}{\lambda_1^{*}} + s\,\frac{\lambda}{\lambda_2^{*}} + t\,\frac{\lambda}{\lambda_3^{*}}\right)$ for the (r, s, t)th order. Extending the method of parts as in Mr. Nath's recent paper, it can easily be seen that the equation giving the amplitudes of successive orders is

$$2\,\frac{d}{dx}\,\phi_{r,s,t}\,(x) = \sigma_1\left\{\phi_{r-1,s,t} - \phi_{r+1,s,t}\right\} + \sigma_2\left\{\phi_{r,s-1,t} - \phi_{r,s+1,t}\right\} + \sigma_3\left\{\phi_{r,s,t-1} - \phi_{r,s,t+1}\right\} \quad \text{where } \sigma_r = \frac{2\pi\mu_r}{\lambda}. \tag{8}$$

The boundary conditions are $\phi_{r,s,t}(0) = 0$, and $\phi_{0,0,0}(0) = 1$.

This can easily be generalised to the case of N systems of sound waves.

To solve the equation

$$2\frac{d}{dz}\phi_{r,s,t}(z) = \sigma_1\left\{\phi_{r-1,s,t} - \phi_{r+1,s,t}\right\} + \sigma_2\left\{\phi_{r,s-1,t} - \phi_{r,s+1,t}\right\} + \sigma_3\left\{\phi_{r,s,t-1} - \phi_{r,s,t+1}\right\} \tag{9}$$

with the conditions $\begin{cases}\phi_{r,s,t}(0) = 0\\ \phi_{0,0,0}(0) = 1.\end{cases}$

Let $\phi_{r,s,t}(z) = \phi\,\dfrac{e^{\rho z}}{\xi_1^{r+1}\xi_2^{s+1}\xi_3^{t+1}}$. This is a solution of the above equation if $2\rho = \sum_{r=1}^{3}\sigma_r\left(\xi_r - \dfrac{1}{\xi_r}\right)$. The most general solution is obtained by summing up similar solutions.

i.e.,

$$\phi_{r,s,t}(z) = \left(\frac{1}{2\pi i}\right)^3 \int\int\int \phi(\xi_1, \xi_2, \xi_3)\, e^{\frac{z}{2}\left\{\sum_{r=1}^{3}\sigma_r\left(\xi_r - \frac{1}{\xi_r}\right)\right\}} \frac{d\xi_1 \cdot d\xi_2 \cdot d\xi_3}{\xi_1^{r+1}\xi_2^{s+1}\xi_3^{t+1}}. \tag{9a}$$

where ϕ is any function of ξ_1, ξ_2, ξ_3. To obtain the solution satisfying the given boundary conditions, we can regard the quantities (ξ_r) as complex variables and take each integral round a closed contour which encircles the orgin once.

The boundary conditions are

$$\begin{cases}(1)\ \phi_{r,s,t}(0) = 0 & r \neq s,\ t \neq 0\\ (2)\ \phi_{0,0,0}(0) = 1\end{cases}$$

$\therefore$ (1) gives $\left(\dfrac{1}{2\pi i}\right)^3 \oint\oint\oint \phi(\xi_1, \xi_2, \xi_3)\,\dfrac{d\xi_1\, d\xi_2\, d\xi_3}{\xi_1^{r+1}\xi_2^{s+1}\xi_3^{t+1}} = 0.$

This implies that $\phi(\xi_1, \xi_2, \xi_3)$ is a constant $= a = 1$ by (2).

$$\therefore\quad \phi_{r,s,t}(z) = \left(\frac{1}{2\pi i}\right)^3 \oint\oint\oint e^{\frac{z}{2}\left\{\sum_{1}^{3}\sigma_r\left(\xi_r - \frac{1}{\xi_r}\right)\right\}} \frac{d\xi_1 \cdot d\xi_2 \cdot d\xi_3}{\xi_1^{r+1}\xi_2^{s+1}\xi_3^{t+1}}.$$

We know that $\dfrac{1}{2\pi i}\oint \dfrac{e^{\frac{\sigma z}{2}\left(\xi - \frac{1}{\xi}\right)}}{\xi^{n+1}}\, d\xi = J_n(\sigma z)$. This can be proved as

follows :

$$\oint \frac{1}{2\pi i} \quad e^{\frac{z}{2}\left(\xi - \frac{1}{\xi}\right)} \frac{d\xi}{\xi^{n+1}} = \text{Residue at the origin.}$$

$$e^{\frac{z}{2}\xi} \cdot e^{-\frac{z}{2\xi}} = \sum_0^\infty \frac{\left(\frac{z}{2}\xi\right)^n}{\lfloor n} \cdot \sum_0^\infty \frac{\left(-\frac{z}{2\xi}\right)^n}{\lfloor n}.$$

Coefficient of ξ^n is given by

$$\left(\frac{z}{2}\right)^n \frac{1}{\lfloor n} - \frac{\left(\frac{z}{2}\right)^{n+2}}{\lfloor 1 \lfloor n+1} + \left(\frac{z}{2}\right)^{n+4} \frac{1}{\lfloor 2 \lfloor n+2} \cdots$$

$$= \left(\frac{z}{2}\right)^n \left\{\frac{1}{\lfloor n} - \frac{\left(\frac{z}{2}\right)^2}{\lfloor 1 \lfloor n+1} + \cdots\right\}$$

$$= \left(\frac{z}{2}\right)^n \left\{\sum_0^\infty (-1)^r \left(\frac{z}{2}\right)^{2r} \frac{1}{\lfloor r \lfloor n+r}\right\}$$

$$= J_n(z).$$

$$\therefore \quad \frac{1}{2\pi i} \oint e^{\frac{z}{2}\left(\xi - \frac{1}{\xi}\right)} \frac{d\xi}{\xi^{n+1}} = J_n(z).$$

$$\therefore \quad \phi_{r,s,t}(z) = \frac{1}{2\pi i} \oint e^{\frac{\sigma_1 z}{2}\left(\xi_1 - \frac{1}{\xi_1}\right)} \frac{d\xi_1}{\xi_1^{r+1}} \cdot \frac{1}{2\pi i} \oint e^{\frac{\sigma_2 z}{2}\left(\xi_2 - \frac{1}{\xi_2}\right)} \frac{d\xi_2}{\xi_2^{s+1}} \times$$

$$\times \frac{1}{2\pi i} \cdot \oint e^{\frac{\sigma_3 z}{2}\left(\xi_3 - \frac{1}{\xi_3}\right)} \frac{d\xi_3}{\xi_3^{t+1}}.$$

$$\therefore \quad \boxed{\phi_{r,s,t}(z) = J_r(\sigma_1 z)\, J_s(\sigma_2 z)\, J_t(\sigma_3 z).} \tag{10}$$

The generalised form of the above equation can be written as

$$2\frac{d}{dz}\phi_{n_1, n_2, \cdots n_N}(z) = \sigma_1 \left\{\phi_{n_1 - 1,\, n_2 \cdots n_N} - \phi_{n_1 + 1,\, n_2, \cdots n_N}\right\}$$

$$+ \sigma_2 \left\{\phi_{n_1,\, n_2 - 1, \cdots n_N} - \phi_{n_1, n_2 + 1, \cdots n_N}\right\} + \cdots$$

$$+ \sigma_N \left\{\phi_{n_1, n_2, \cdots n_{N-1}} - \phi_{n_1, n_2, \cdots n_N + 1}\right\}. \tag{11}$$

where $n_1, n_2, \cdots n_N$ are integers and $\{\sigma_r\}$ are constants. $\left(\sigma_r = \frac{2\pi\mu_r}{\lambda}\right)$.

Proceeding as before, we have the general solution given by

$$\phi_{n_1, n_2, \cdots n_N}(z) = \left(\frac{1}{2\pi i}\right)^N \underbrace{\int\int \cdots \int\int}_{N} \phi(\xi_1, \xi_2 \cdots \xi_n) \cdot e^{\frac{z}{2}\left\{\sum_{r=1}^{N} \sigma_r \left(\xi_r - \frac{1}{\xi_r}\right)\right\}} \times \frac{d\xi_1 \cdot d\xi_2 \cdots d\xi_N}{\xi_1^{n_1+1} \xi_2^{n_2+1} \cdots \xi_N^{n_N+1}}. \tag{11a}$$

To obtain the solution satisfying the boundary conditions

$$\left.\begin{aligned} \phi_{n_1, n_2, \cdots n_N}(0) &= 0 \\ \phi_{0,0,\cdots 0}(0) &= 1 \end{aligned}\right\}$$

we regard the quantities (ξ_r) as complex variables and integrate them round contours enclosing the origin once. We therefore get,

$$\phi_{n_1, n_2, \cdots n_N}(z) = \left(\frac{1}{2\pi i}\right)^N \underbrace{\oint\oint \cdots \oint\oint}_{N} e^{\frac{z}{2}\left\{\sum_1^N \sigma_r \left(\xi_r - \frac{1}{\xi_r}\right)\right\}} \cdot \frac{d\xi_1 \cdot d\xi_2 \cdots d\xi_N}{\xi_1^{n_1+1} \cdot \xi_2^{n_2+1} \cdot \xi_N^{n_N+1}}.$$

$$= \prod_{r=1}^{N} \left\{ \frac{1}{2\pi i} \oint e^{\frac{\sigma_r z}{2}\left(\xi_r - \frac{1}{\xi_r}\right)} \frac{d\xi_r}{\xi_r^{n_r+1}} \right\}.$$

$$= J_{n_1}(\sigma_1 z) \cdot J_{n_2}(\sigma_2 z) \cdots J_{n_N}(\sigma_N z).$$

$$\boxed{\phi_{n_1, n_2, \cdots n_N}(z) = \prod_{r=1}^{N} J_{n_r}(\sigma_r z).} \tag{12}$$

$$\text{Intensity} = |\phi_{n_1, n_2, \cdots n_N}(z)|^2 = \prod_{r=1}^{N} J_n^2(\sigma_r z). \tag{13}$$

This same expression has been obtained by E. Fues by applying the simplified theory of Raman-Nath (R.-N. I). In conclusion it is my greatest pleasure to record my respectful thanks to Professor Sir C. V. Raman, for suggesting the present investigation and for much valuable guidance and criticism in the course of the work.

5. *Summary.*

The results of Raman and Nath in their general theory of the diffraction light by ultrasonic waves at normal and oblique incidences are shown to be in complete agreement with those of Van Cittert for the case of normal incidence and also with those obtained by extending Van Cittert's method to the case of oblique incidence. The amplitude function for the latter case is developed *in extenso* in a series of Bessel functions. The expression for the

intensity with normal incidence in the case of N systems of sound waves is $|J_{n_1}(\sigma_1 z) J_{n_2}(\sigma_2 z) \cdots J_{n_N}(\sigma_N z)|^2$, where $n_1, n_2, \cdots n_N$ are the orders excited. This result is the same as that which has been obtained by E. Fues by applying the simplified Raman-Nath method to the case considered.

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ON LINEAR TRANSFORMATIONS OF BOUNDED SEQUENCES—III.

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PART III.

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§ 13. *General Remarks.*

This part deals with a subclass of T [T as defined in 2·1 of Part I of this paper]. We designate the direct and inverse transformations of this class by U and U^{-1}, and prove that these transformations, and others defined by their products are commutative. We further shew that transformations corresponding to differences of any real order form a subclass of the group defined by U, U^{-1}, and their products. In (16) we shew that some important theorems of Anderson (A. 1)* are, either deducible from, or particular cases of, theorems of Parts I and II of this paper. In (17) we discuss the generalization of Knopp's results on "Mehrfach monotone folgen" (K · 2).†

§ 14. *A Class of Commutative Transformations.*

Let $\| a_{m,n} \|$ define a U. Then besides the four conditions of (2·1) of Part I, condition (*e*), namely, $a_{n,n+p} = a_p$ for all n, *i.e.*, $a_{0p} = a_{1,p+1} = a_{n,n+p} = \cdots$, characterizes a_{mn}; so that $a_{m,n}$ for U is characterized as follows:

$$(a')\ a_{n,n} = 1 \quad (b')\ a_{mn} = 0,\ n < m \quad (c')\ a_p \leqslant 0 \text{ for all } p \geqslant 1 \qquad [14\cdot1]$$

$(d')\ -\sum_{p=1}^{\infty} a_p \leqslant 1$. We see that a U is defined completely by a sequence $\{a_p\}$ satisfying (c') and (d').

(A·1)*. A. F. Anderson *Studier over Cesaro's summabilitets methode* (Danish). See the second chapter entitled "Om differencer".

(K·2)†. K. Knopp, "Mehrfach Monotone folgen," *Mathematisssche Zeitschrift*, 1925, 22, 75-85.

In section 2 of Part I we established the existence of a unique reciprocal matrix $\| \beta_{m,n} \|$ such that $\| \beta_{m,n} \| \cdot \| a_{m,n} \| = \| \delta_{m,n} \|$ (unit matrix). Since any U is a T it follows that in this case also $\| \beta_{m,n} \|$ the reciprocal matrix exists.

Further from section 2 of Part I, we obtain

$$\beta_{n,n+\rho} = - \sum_{k=1}^{\rho} a_{n,n+k} \cdot \beta_{n+k,n+\rho} \quad (2 \cdot 6)$$

We can at once deduce $\beta_{n,n+\rho} = b_\rho$ for all n ; and

$$b_\rho = - \sum_{k=1}^{\rho} a_k \, b_{\rho-k}. \qquad [14 \cdot 2]$$

We obtain the following results also easily. $b_0 = 1$, $b_n > 0$, and from $(14 \cdot 2)$ it follows that b_n is given by the equation

$$(\sum_{0}^{\infty} b_n \, x^n) \cdot (1 + \sum_{n=1}^{\infty} a_n \, x^n) = 1. \qquad [14 \cdot 3]$$

If U_1 and U_2 are defined by $\{a_n^1\}$ and $\{a_n^2\}$, it is easy to prove
(1) $U_1 U_2 = U_2 U_1$; (2) if $\| c_{m,n} \|$ defines $U_1 U_2$ then $c_{n,n+\rho} = a_\rho^3$ for all n,
(3) a_ρ^3 is given by the equation

$$1 + \sum_{\rho=1}^{\infty} a_\rho^3 \, x^\rho = (1 + \sum_{1}^{\infty} a_\rho^1 \, x^\rho)(1 + \sum_{1}^{\infty} a_\rho^2 \, x^\rho). \qquad [14 \cdot 4]$$

The matrix of any product of U's and U^{-1}'s is always characterized by condition (e) of $14 \cdot 1$. If $\{a_\rho\}$ defines the product a_ρ can be calculated in all cases from an equation of the type of $(14 \cdot 4)$. It is quite easy to shew that the commutative property is true for any product of U's and U^{-1}'s.

§ 15. *Differences of any Real Order.*

THEOREM : Transformations defined by differences of any real order form a subclass of the class formed by U's, U^{-1}'s, and their products.

Lemma 1. If $0 \leqslant \gamma \leqslant 1$ then we shall prove that $\Delta^\gamma \equiv U(\gamma)$.

Formally the difference

$$\Delta^\gamma v_n = v_n - \gamma v_{n+1} + \frac{\gamma(\gamma-1)}{\lfloor 2} v_{n+2} - \frac{\gamma(\gamma-1)(\gamma-2)}{\lfloor 3} v_{n+3} + \cdots$$

$$= v_n - \gamma v_{n+1} - \frac{\gamma(1-\gamma)}{\lfloor 2} v_{n+2} - \cdots - \frac{\gamma(1-\gamma)\cdots(p-1-\gamma)}{\lfloor p} v_{n+p} - \cdots$$

Consider a transformation $U(\gamma)$ defined by $\{a_n\}$ as follows :

$$a_1 = -\gamma \quad a_2 = -\frac{\gamma(1-\gamma)}{\lfloor 2} \quad \cdots \quad a_p = -\frac{\gamma(1-\gamma)(p-1-\gamma)}{\lfloor p}$$

then, $a_p < 0$ for $p \geqslant 1$ and $-\sum_{1}^{\infty} a_p = 1$.

Hence conditions (c') and (d') of $(14\cdot1)$ are fulfilled and we have

$$\Delta^{\gamma} \equiv \mathrm{U}(\gamma). \qquad [15\cdot1]$$

Lemma 2. If $0 \leqslant \gamma \leqslant 1 \qquad \Delta^{-\gamma} = \{\mathrm{U}(\gamma)^{-1}\}$ $[15\cdot2]$

By $(14\cdot3)$ this is obvious.

Proof of Theorem : Let $\mathrm{U}(1) \equiv \Delta^{1}$ as in $(15\cdot1)$

Let $[\mathrm{U}(1)]^{-1} \equiv \Delta^{-1}$ as in $(15\cdot2)$

Then if Δ^{p} be a difference of any positive order, consider the transformation

$$\mathrm{S} = [\mathrm{U}(1)]^{m} \cdot \mathrm{U}(\gamma)$$

where $m = [p]$ and $\gamma = (p)$

and $\mathrm{U}(\gamma) \equiv \Delta^{\gamma}$.

If $\{a_{\rho}\}$ defines S, it is given as in $(14\cdot4)$ by

$$1 + \Sigma a_{\rho} x^{\rho} = (1-x)^{m} \cdot \left(1 - \gamma x - \gamma \frac{(1-\gamma)}{\lfloor 2} x^{2} \cdots\right)$$

$$= (1-x)^{m+\gamma} = (1-x)^{p}$$

so that $a_{n} = (-1)^{n} \dfrac{p\,(p-1)\,(p-n-1)}{\lfloor n}$

i.e., $\mathrm{S} \equiv \Delta^{p} \equiv [\mathrm{U}(1)]^{m}\ \mathrm{U}(\gamma)$. $[15\cdot3]$

If p is negative we prove in exactly the same way as above

$$\Delta^{p} \equiv \{[\mathrm{U}(1)]^{-1})\}^{m} \cdot \{\mathrm{U}(\gamma)\}^{-1}$$

where $m = (-p)$ and $\gamma = (-p)$. $[15\cdot4]$

Hence the theorem.

§ 16. *Deductions of Some Theorems of Anderson.*

We propose in this section to derive Soetning 3, 4, and 5 of Anderson on differences from theorems of Part I and II of this paper.

Soetning III (page 20 of Anderson's Book A·1).

(*a*) If $x_{n} = \mathrm{O}(1) \quad r > 0 \quad s > -1$ and $r + s > 0$

then $\Delta^{s}\{\Delta^{r}(x_{n})\} = \Delta^{r+s}(x_{n})$

(*b*) If $x_{n} = 0(1) \quad r > 0 \quad s \geqslant -1$ and $r + s \geqslant 0$

then $\Delta^{s}\{\Delta^{r}(x_{n})\} = \Delta^{r+s}(x_{n})$.

Proof of (*a*) : Leaving aside the trivial case of $s > 0$ we shall shew that (*a*) is a particular case of Theorem XVIII of section 11§, Part II of this paper.

Let $s < 0$ and $s = -q \quad q < 1$ choose q_{1} such that $q < q_{1} < 1$ and $q_{1} < r$ so that $r = q_{1} + t, \ t > 0$.

Then by Theorem of 15§ $\Delta^{t} \equiv \mathrm{U}_{\rho_{1}} \cdot \mathrm{U}_{\rho_{2}} \cdot\cdot\, \mathrm{U}_{\rho_{k}}$

and $\Delta^{r} = \mathrm{U}(q_{1}) \cdot \mathrm{U}_{\rho_{1}} \cdots \mathrm{U}_{\rho_{k}}$

where $\mathrm{U}(q_1) = \Delta^{q_1}$ as in (15·1)

and $\Delta^s = [\mathrm{U}(q)]^{-1}$.

Since $\{x_n\}$ is bounded by Theorem II of Part I so is $(\mathrm{U}_{\rho_1}\, \mathrm{U}_{\rho_2}\, \mathrm{U}_{\rho_k})\,(x_n) = y_n$.

We shall now shew that $[\mathrm{U}(q)]^{-1} \cdot [\mathrm{U}(q_1)\,(y_n)] = \{[\mathrm{U}(q)]^{-1} \cdot \mathrm{U}(q_1)\}\,(y_n)$.

Let $\| \beta_{mn} \|$ define $[\mathrm{U}(q_1)]^{-1}$ and $\| s_{mn} \|$ define $[\mathrm{U}(q)]^{-1}$

then $s_{n,n+p} = s_p = \dfrac{q(q+1)(q+p-1)}{\lfloor p} = \mathrm{O}(p^{q-1})$

and $\beta_{n,n+p} = b_p = \dfrac{q_1(q_1+1)(q_1+p-1)}{\lfloor p} = 0(p^{q_1-1})$

therefore $\dfrac{s_{n,n+p}}{\beta_{n,n+p}} = 0(p^{q-q_1}) \quad \therefore \quad \dfrac{s_{n,n+p}}{\beta_{n,n+p}} \to 0$ as $p \to \infty$

Obviously s_p is bounded and y_n bounded. Hence the three conditions of Theorem XVIII are fulfilled and we have

$$[\mathrm{U}(q)]^{-1} \cdot [\mathrm{U}(q_1)\,(y_n)] = \{[\mathrm{U}(q)]^{-1} \cdot \mathrm{U}(q_1)\}\,(y_n) = \Delta^{q_1 - q}\, y_n$$
$$= \mathrm{U}(q_1 - q)\,(y_n).$$

But $y_n = \mathrm{U}_{\rho_1} \cdots \mathrm{U}_{\rho_k}(x_n)$

and by Theorem II of Part I

$$[\mathrm{U}(q_1 - q)]\,[\mathrm{U}_{\rho_1}\, \mathrm{U}_{\rho_2}\, \mathrm{U}_{\rho_k}(x_n)] = [\mathrm{U}(q_1 - q) \cdot \mathrm{U}_{\rho_1} \cdots \mathrm{U}_{\rho_k}]\,(x_n)$$
$$= \Delta^{r+s}(x_n).$$

Proof of (*b*) : Leaving aside the trivial case of $s > 0$, this is a particular case of Theorem X of section 8§, Part II (refer 8·32).

Let $s = -q \quad q > 0 \quad r = q + t \quad t \geqslant 0$

then $\Delta^s = [\mathrm{U}(q)]^{-1}$ and $\Delta^r = \Delta^q \cdot \Delta^t$

$$= \mathrm{U}(q) \cdot \mathrm{U}_{\rho_1}\, \mathrm{U}_{\rho_2} \cdots \mathrm{U}_{\rho_k}.$$

Since x_n is a null sequence by 8·32 of Part II

$$[\mathrm{U}(q)]^{-1}\,[\mathrm{U}(q)\, \mathrm{U}_{\rho_1}\, \mathrm{U}_{\rho_2} \cdots \mathrm{U}_{\rho_k}(x_n)] = \mathrm{U}_{\rho_1}\, \mathrm{U}_{\rho_2} \cdots \mathrm{U}_{\rho_k}(x_n)$$

or

$$\Delta^s\,[\Delta^r(x_n)] = \Delta^{r+s}(x_n).$$

Statement Soetning IV and V of Anderson :—

Soetning IV (*a*)—If, $x_n = \mathrm{O}\left(\dfrac{1}{n^a}\right)$, $a > 0, r > -a,\ s > -1-a,\ r+s > -a$

then $\Delta^s\,[\Delta^r(x_n)] = \Delta^{r+s}(x_n)$.

Soetning IV (*b*)—If $x_n = 0\left(\dfrac{1}{n^a}\right)$, $a > 0\ r > -a, s \geqslant -1-a, r+s > -a$

then $\Delta^s\,[\Delta^r(x_n) = \Delta^{r+s}(x_n)$.

Soetning V (*c*)—If $x_n = 0\left(\dfrac{1}{n^a}\right)$, $a > 0$, $r > -a$, $s \geqslant -1-a$, $r+s \geqslant -a$

$\Delta^s\,[\Delta^r(x_n)] = \Delta^{r+s}(x_n)$ when the latter exists.

We shall shew that these are particular cases of Theorems VI, VII, VIII and IX of Part II of this paper. There is a considerable amount of overlapping of the various cases occurring in (a), (b), (c). In any particular case of (a) we shall have

(a') $s \geqslant -1-a_2$, $r \geqslant -a_2$, and $r+s \geqslant -a_2$, where $0 < a_3 < a$.

The cases of (b) which do not occur under (a) are

(b') $s = -1-a$, $r > -a$, $r+s > -a$.

The cases of (c) which do not occur under (a) and (b) are

(c') $r+s = -a$, $r > -a$, $s \geqslant -1-a$.

We propose to further divide (a'), (b') and (c') as follows :

(a') :— (a_1') when $s \geqslant -a_2$; (a_2') $s = -a_2 - q$ $0 \leqslant q \leqslant 1$

(b') :— only one case (b'_1)

(c') :— (c_1') when r and s are negative

i.e., $r = -a_3$ $s = -a_4$ $a_3 > 0$ $a_4 > 0$ and $a_3 + a_4 = a$

(c_2') when $0 \leqslant r \leqslant 1$ and $s = -a-r$.

We shall shew that (a_1') is a particular case of Theorem VII of Part II

(a'_2), (b_1') and (c_2') are particular cases of Theroem IX of Part II

and (c_1') is a particular case of Theorem VI of Part II.

Proof : (a_1') $r \geqslant -a_2$ $s \geqslant -a_2$ and $r+s \geqslant -a_2$.

By 15·4 $\Delta^{-a_2} = U_1^{-1} \cdot U_2^{-1} \cdots U_k^{-1}$ and the most general way of taking Δ^r and Δ^s would be $\Delta^r = (U_1^{-1} \cdot U_2^{-1} \cdot U_l^{-1} U_{\rho_1} \cdot U_{\rho_2} \cdots U_{\rho_r})$ and $\Delta^s = (U_{q_1} U_{q_2} \cdots U_{q_s} \cdot U_{l+1}^{-1} \cdot U_{l+2}^{-1} \cdots U_k^{-1})$.

If $\| \beta_{n, n+p} \|$ defines $(U_1^{-1} \cdots U_k^{-1})$ then $\beta_{n, n+p} = b_p =$

$$\frac{a_2 (a_2+1) \cdots (a_2+p-1)}{\lfloor p} = O(p^{a_2-1})$$

and $$\sum_{\rho=0}^{n} b_\rho = B_n = O(n^{a_2})$$

Let $a_2 (1+\delta) = a$; since $a_2 < a$ $\delta > 0$;

By hypothesis $$x_n = O\left(\frac{1}{n^a}\right) = O\left(\frac{1}{B_n^{1+\delta}}\right).$$

Hence by (8·20) of Theorem VII of Part II

$$\Delta^s [\Delta^r (x_n)] \equiv (U_{q_1} U_{q_2} \cdot U_{q_s} \cdot U_{l+1}^{-1} \cdots U_k^{-1}) [(U_1^{-1} \cdots U_l^{-1} U_{\rho_1} \cdots U_{\rho_r} (x_n)]$$
$$= (U_{q_1} \cdots U_{q_r} \cdot U_{l+1}^{-1} \cdots U_k^{-1} \cdots U_1^{-1} \cdot U_l^{-1} U_{\rho_1} \cdots U_{\rho_r}) (x_n) = \Delta^{r+s} (x_n).$$

Proof of (a_2') : $s = -a_2 - q$ $0 \leqslant q \leqslant 1$ $r = q+t$ $t \geqslant 0$

since $$x_n = O\left(\frac{1}{n^a}\right) \text{ as above } x_n = O\left(\frac{1}{B_n^{1+\delta}}\right) = 0\left(\frac{1}{B_n}\right).$$

Let $\Delta^{-\alpha_2} = U_1^{-1} \cdots U_k^{-1}$.

$\Delta^q = U(q)$

then $\Delta^s = (U_1^{-1} \cdots U_k^{-1})\,[U(q)]^{-1}$

$\Delta^r = U(q)\, U_{\rho_1} \cdot U_{\rho_2} \cdots U_{\rho_r}$.

If $\| \beta_{n, n+p} \|$ defines $(U_1^{-1} \cdots U_k^{-1})$ and $b_\rho = \beta_{n, n+p}$ and $B_n = \sum_{\rho > 0}^{n} b_\rho$

since by hypothesis $x_n = 0\left(\frac{1}{B_n}\right)$ we have by (8·30) and (8·31) of Theorem IX of Part II

$$\Delta^s[\Delta^r(x_n)] \equiv [U_1^{-1} \cdots U_k^{-1}\{U(q)\}^{-1}]\,(U(q)\, U_{\rho_1} U_{\rho_2} \cdots U_{\rho_r})\,(x_n)$$
$$= (U_1^{-1} \cdots U_k^{-1} \cdot U_{\rho_1} U_{\rho_r})\,(x_n)$$
$$= \Delta^{r+s}(x_n) \text{ when the latter exists.}$$

But the latter exists by Theorem VII since $x_n = O\left(\frac{1}{B_n^{1+\delta}}\right)$, $\delta > 0$

Hence (a_2') is established.

Proof of (b'): $s = -1 - \alpha \quad r = 1 + t \quad t > 0 \quad x_n = 0\left(\frac{1}{n^\alpha}\right)$

Let $\Delta^1 = U(1)$, $\Delta^{-\alpha} = (U_1^{-1} \cdots U_k^{-1})$

then if $\| \bar{\beta}_{mn} \|$ defines $(U_1^{-1} \cdots U_k^{-1})$ $\beta_{n, n+p} = b_p$

$$= \frac{\alpha(\alpha+1)(\alpha+p-1)}{\lfloor p} = 0(p^{\alpha-1})$$

and $B_n = \sum_{\rho=0}^{n} b_\rho = 0(n^\alpha)$.

We therefore have $\Delta^r = U(1) \cdot U_{\rho_1} U_{\rho_2} \cdots U_{\rho_r}$.

$\Delta^s = [U(1)]^{-1} U_1^{-1} U_k^{-1}$

and since $x_n = 0\left(\frac{1}{B_n}\right)$

$\Delta^s[\Delta^r(x_n)] = [\{U(1)\}^{-1} \cdot U_1^{-1} \cdots U_k^{-1}]\,[U(1) \cdot U_{\rho_1} \cdots U_{\rho r}]$

$= (U_1^{-1} \cdots U_k^{-1} \cdot U_{\rho_1} \cdots U_{\rho_r})\,(x_n) = \Delta^{r+s}(x_n)$ if the latter exists by (8·30) and (8·31) of Theorem IX of Part II.

But the latter exists since $x_n = 0\left(\frac{1}{n^\alpha}\right)$ and $r + s > -\alpha$ by Theorem VII.

Proof of (c_2'): In this case argument is identical with that of (b') except in the last step where it must be noted that the equality will be valid if $\Delta^{-\alpha} x_n$ exists.

Proof of (c'_1): $r = -\alpha_3 \quad s = -\alpha_4 \quad \alpha_3 + \alpha_4 = \alpha \quad \alpha_3 > 0 \quad \alpha_4 > 0 \quad x_n = 0\left(\frac{1}{n^\alpha}\right)$

Let $\| \beta_{n,\rho} \|$ define $\Delta^{-\alpha_3}$. We shall prove that

$$\left| \sum_{\rho=A}^{\infty} \beta_{n,\rho} \mid x_\rho \mid \right| = 0\left(\frac{1}{A^{\alpha_4}}\right)$$

Proof: $\beta_{n,n+\rho} = b_\rho = 0\,(p^{\alpha_3 - 1})$ and $\sum^{n} b_\rho = B_n = O\,(n^{\alpha_3})$

and $x_n = \dfrac{\epsilon\,(n)}{n^{\alpha}} = \dfrac{\epsilon\,(n)}{n^{\alpha_3(1+\delta)}} = \dfrac{\epsilon\,(n)}{B_n^{1+\delta}}$ where $\epsilon\,(n) \to 0$ as $n \to \infty$.

Hence by result (1) of Theorem VII.

$$\left| \sum_{\rho=A}^{\infty} \beta_{n,\rho} \mid x_\rho \mid \right| \leqslant \frac{\epsilon^1\,(A)}{B_A^{\delta}} = \frac{\epsilon'\,(A)}{A^{\alpha_4}} = 0\left(\frac{1}{A^{\alpha_4}}\right).$$

If $\| \beta'_{n,\rho} \|$ defines $\Delta^{-\alpha_4}$ then $\beta'_{n,n+\rho} = b_\rho' = O\,(p^{\alpha_4 - 1})$

and $\sum^{n} b_\rho' = B_n' = O\,(n^{\alpha_4})$.

Hence $\left| \sum_{A}^{\infty} \beta_{n,\rho} \mid x_\rho \mid \right| = 0\left(\dfrac{1}{B_A'}\right)$ uniformly for all n.

Hence the conditions of Theorem VI are fulfilled and we have by the same theorem

$$\Delta^{-\alpha_4}\,[\Delta^{-\alpha_3}\,(x_n)] = \Delta^{-\alpha}\,(x_n) \text{ when the latter exists.}$$

§ 17. *Generalization of some Theorems of Knopp.*

His results in the paper (K. 1) are as follows:

Given $x_n > 0$ and $x_n = 0\,(1)$ then

I. If $\Delta^{\alpha}\,(x_n) \geqslant 0$ for all n, then $\Delta^{\beta}\,(x_n) \geqslant 0$ for $0 \leqslant \beta \leqslant \alpha$. (Satze 6 of his paper).

II. If $\alpha \geqslant 1$ and $0 \leqslant \beta \leqslant \alpha - 1$ and $x_n > 0$ $x_n = 0\,(1)$ and $\Delta^{\alpha}\,(x_n) > 0$ for all n

then $\Delta^{\beta}\,(x_n) = 0\left(\dfrac{1}{n^{\beta}}\right)$ [Satze 9 of his paper]

and two particular cases of II are also given as Satze 7 and Satze 8 of his paper.

It will be shewn that,

$$\text{if } \alpha > 0 \quad (x_n) = y_n \quad y_n > 0$$

$$\text{then for all } 0 \leqslant \beta \leqslant \alpha \quad \Delta^{\beta}(x_n) = \Delta^{-(\alpha-\beta)}\,(y_n) \qquad [17\cdot1]$$

and in particular $x_n = \Delta^{-\alpha}\, y_n$, is an immediate consequence of Theorem IV of Part I.

In particular $x_0 = \Delta^{-\alpha} y_0 = \Sigma\, A_n^{\alpha-1}\, \Delta^{\alpha}\,(x_n) = \Sigma\, A_n^{\alpha-1} \mid \Delta^{\alpha}\,(x_n) \mid$. Hence the conditions of Hjaelpsoetning III. B of Anderson on page 34 of his book (A·1) are satisfied and result II of Knopp follows at once as a particular

case of the theorem of Anderson. It is rather remarkable that Knopp has not noticed this. We will here give generalizations of results I and II applicable to U's.

THEOREM I : Let $S = U_1 U_2 \cdot U_3 \cdot U_k$ and $S(x_n) = y_n$

and $S' = U_{r+1} \cdot U_{r+2} \cdots U_k$ and $S'(x_n) = z_n$

If $x_n = 0(1)$ and $y_n > 0$ for all n,

then $S'(x_n) = (U_1^{-1} U_2^{-1} \cdots U_r^{-1})(y_n)$

and $S'(x_n) > 0$ for all n [17·2]

Proof : $y_n = S(x_n) = (U_1 U_2 U_r)(U_{r+1} \cdots U_k)(x_n)$

$= (U_1 U_2 U_r)\{S'(x_n)\}$ by Theorem II of Part I

$= (U_1 U_2 U_r)(z_n)$.

Also since $x_n = 0(1)$ so is $z_n = 0(1)$ by Theorem II of Part I.

Hence by repeated application of Theorem IV of Part I just as in the corollary to it.

$$z_n = (U_r)^{-1} \cdot (U_{r-1})^{-1} \cdots (U_1)^{-1}(y_n)$$

$$= \Sigma \beta^r{}_{n,\, n+p_1} \cdot \Sigma \beta^{r-1}{}_{n+p_1,\, n+p_2} \cdots \Sigma \beta'{}_{n+p_{r-1},\, n+p} y_{n+p} \qquad [17\cdot3]$$

where $\| \beta^r{}_{m,n} \|$ defines $(U_r)^{-1}$. The multiple series on the right can be summed up in any manner since $\beta_{m,n} \geqslant 0$ and $y_n \geqslant 0$.

$$\therefore \quad z_n = (\Sigma \beta^r{}_{n,\, n+p_1} \cdot \beta^{r-1}{}_{n+p_1 \cdot n+p_2} \cdots \beta'{}_{n+p_{r-1},\, n+p}) \cdot y_{n+p}$$

$$= \sum_{p=0}^{\infty} \bar{\beta}_{n+p} y_{n+p}$$

where $\| \bar{\beta}_{m,n} \| = \| \beta^r{}_{m,n} \| \cdot \| \beta^{r-1}{}_{m,n} \| \cdots \| \beta'{}_{m,n} \|$.

Hence $z_n = (U_1^{-1} \cdot U_2^{-1} \cdots U_r^{-1})(y_n) = (U_{r+1} \cdots U_k)(x_n)$

since $y_n > 0$ and all $\bar{\beta}_{mn} \geqslant 0$ we have $z_n > 0$

and in particular we have $x_n' = (U_1^{-1} \cdots U_k^{-1})(y_n)$, when $r = k$. [17·4]

When the U's are Δ's we have as a deduction from above the result of (17·1) namely :—If $\Delta^{\alpha}(x_n) = y_n > 0$ for all n $\alpha > 0$

then $\Delta^{\beta}(x_n) = \Delta^{-(\alpha-\beta)} y_n$

and in particular $x_n = \Delta^{-\alpha} y_n$.

THEOREM II : Let $U(1) \equiv \Delta^1$ and $S = [U(1) \cdot U_1 U_2 U_3 U_k]$

$S' = U_1 U_2 \cdots U_k$.

Let $\| \bar{\beta}_{m,n} \|$ define $U_1^{-1} U_2^{-1} \cdots U_k^{-1}$

Now $\bar{\beta}_{n,n+p} = b_p$. Let $\sum_0^n b_p = B_n$

then if

$x_n = 0(1)$ and $S(x_n) = y_n$ be > 0 for all n, then $S'(x_n) = 0\left(\frac{1}{B_n}\right)$. [17·5]

Proof: By 17·4 $x_n = [\{U(1)\}^{-1} \cdot U_1^{-1} \cdot U_2^{-1} \cdots U_k^{-1}](y_n)$

$$= \{U(1)\}^{-1} \cdot (U_1^{-1} \cdots U_k^{-1})(y_n)$$

$$= U(1)^{-1} \cdot (\Sigma \beta_{n,\, n+\rho}\, y_{n+\rho})$$

$$= U(1)^{-1} \left(\sum_0^\infty b_\rho \cdot y_{n+\rho}\right)$$

$$= \sum_0^\infty B_\rho\, y_{n+\rho}$$

and $$x_0 = \sum_0^\infty B_\rho\, y_\rho$$

and $$S'(x_n) = [U(1)]^{-1}(y_n) = \sum_n^\infty y_\rho.$$

Now $$\sum_n^\infty y_\rho = \sum_n^\infty \frac{B_\rho\, y_\rho}{B_\rho} \leqslant \frac{1}{B_\rho} \cdot \Sigma B_\rho \cdot y_\rho = 0\left(\frac{1}{B_n}\right)$$

since $\Sigma B_\rho\, y_\rho$ converges and $B_0 \leqslant B_1 \leqslant \cdots \leqslant B_n \leqslant \cdots$

Hence $$S'(x_n) = 0\left(\frac{1}{B_n}\right).$$ Thus proving (17·5).

Result II of Knopp follows immediately from this

for let $U(1) = \Delta^1 \quad U_1 U_2 U_k = \Delta^\alpha \quad \alpha > 0$

If $$\Delta^{1+\alpha}(x_n) > 0 \text{ for all } n$$

then $$\Delta^\alpha x_n = 0\left(\frac{1}{n^\alpha}\right)$$

for B_n in this case $= O(n^\alpha)$.

Knopp's Satze 7 is an immediate consequence of this. His Satze 8 takes the following interesting form in terms of U's.

If $U(x_n) = y_n$ be > 0 for all n, $x_n > 0$ and $x_n = 0(1)$ and $\sum_0^\infty x_n$ convergent, then,

$B_n x_n \to 0$ as $n \to \infty$ where $\{b_n\}$ defines U^{-1} as in (14·3) and $B_n = \sum_{\rho=0}^{n} b_\rho$. Putting $r_n = x_n + x_{n+1} + \cdots$

we have $$\Delta r_n = x_n = U(1)(r_n).$$

Hence $$[U(1) \cdot U](r_n) = y_n > 0 \quad \text{for all } n.$$

Hence $$U(r_n) = 0\left(\frac{1}{B_n}\right) \text{ by } (17 \cdot 5).$$

But $U(r_n) = \sum_n^\infty x_\rho + a_1 \sum_{n+1}^\infty x_\rho + a_2 \sum_{n+2}^\infty x_\rho + \cdots$, where $\{a_n\}$ defines U

The right-hand side is an absolutely convergent double series since

$$\sum_1^\infty |a_n| = -\sum_1^\infty a_n \leqslant 1 \text{ and } \Sigma x_n \text{ is convergent.}$$

Hence $\quad U(r_n) = x_n + x_{n+1}(1 + a_1) + x_{n+2}(1 + a_1 + a_2) + \cdots$

since $1 + a_1 + a_2 + a_n > 0$ by condition (d') of 14·1

we have $x_n < U(r_n)$

Hence

$$x_n = 0\left(\frac{1}{B_n}\right). \qquad [17\cdot6]$$

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Erratum.

Vol. VIII, No. 1, *page* 55, *line* 31.

Instead of " These interactions are the ' exchange effects ' . . . ."
read " These interactions are not the ' exchange effects ' . . . ."